

A HIGHER SCHOOL CHEMISTRY

BY

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PREFACE

THIS book is intended to cover the work for the usual School Certificate, and to meet the requirements of examinations of the standard of the London Matriculation Army Entrance, Oxford and Cambridge Senior Locals, Scottish Universities Entrance, and Scottish Higher Leaving Certificate.

Experiments are freely interspersed with the text, and suggestions for a few additional experiments will be found at the end of each chapter.

As the capability of a student is still—and will probably continue for many years to be—judged mainly by his ability to pass written examinations, questions have been attached to each chapter in order that he may realise what is expected of him.

Thanks are due to the University of London, the Oxford and Cambridge Schools Examination Board, the Scottish Universities Entrance Board, and the Scottish Education Department, for permission to reproduce a selection of questions from their respective Examination Papers.

The help of Mr. James Sandilands of the Heriot-Watt College, of Mr. John Melville of George Heriot's School, of Mr. J. W. Swanney of Boroughmuir School, and of Mr. A. Buchan of Biggar School, in suggestion, revision, and correction, is also gratefully acknowledged.

J. CAMPBELL SMITH.

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CHAPTER I

INTRODUCTION. EARLY HISTORY OF CHEMISTRY

THE questions are sometimes asked, 'Why should I study Chemistry?' 'Of what use will Chemistry be to me?'

Do we ever realise how at every turn of our daily lives we come in contact with Chemistry and its achievements? Just think for a moment of your daily routine, how few of the things you use and handle are purely natural products, how many of them have been prepared by chemical processes.

You rise in the morning, go to the bathroom and wash yourself. The water tap which you turn on may be of brass, an alloy of copper and zinc, or perhaps of that useful material stainless steel, which contains iron, nickel and chromium. The wash-hand basin has been made from a mixture of different clays, the enamel on its surface compounded from a chemical formula. In the manufacture of your soap from fats, caustic soda and sodium chloride have been used. Your tooth powder is chalk chemically coloured and flavoured. The clothes in which you dress yourself, whether they be of wool, cotton, or linen, have been chemically treated. The raw material has probably been cleaned by sulphuric acid and alkali, and bleached by chlorine or sulphur dioxide. Your buttons, which once might have been natural bone or horn, are now of metal or celluloid, or may have even been made from cheese. You knot your tie, which, if it is silk, is likely artificial and made from wood pulp, and its brilliant colours along with those of your cap and blazer are probably due to aniline dyes derived from coal tar. The skins of animals, of course, provide the leather for your shoes, but this must be tanned by a chemical process.

You sit down to breakfast. The laws against the adulteration of foods are so strict that we hope your breakfast table will be free from chemicals. But look a little deeper. Your

porridge, if you begin with this wholesome fare, comes from oats grown with the assistance of chemical fertilisers. The cow that produced your milk may have been partly fed on chemical foods. Your bread owes its lightness and porosity to carbon dioxide gas. The butter is probably pure except for a trace of colouring matter. If it is an Empire product it has crossed the sea from New Zealand in cold storage rooms kept cool by a chemical process. If you use margarine, part of the fat in it may have been made from vegetable oils by the action of hydrogen. And so on. The influence of Chemistry follows you all through your daily work and play, you cannot get away from it.

Turning to larger things, engineering science could never have produced its marvels of construction without the assistance of the chemist in providing suitable material. The efficiency of the present-day motor-car, speed-boat and aeroplane is largely due to assiduous chemical research in devising light and strong metallic alloys. The wireless valve which brings the ends of the earth to our firesides, the brilliant neon signs which illuminate our city streets, the invisible ray which sounds its own alarm, are only a few of the modern marvels of the application of Chemistry, in co-operation with Physics, for the benefit of mankind.

These examples are sufficient to show how Chemistry, more than any other science, has woven itself into the warp and woof of our daily lives, and for this reason alone, apart from the fact that it is a fascinating study, we are all the better of having some knowledge of this ancient and useful branch of learning.

Early History of Chemistry. In Chemistry, experiment must precede and prepare the way for theory. So it has been in chemical history. The earliest information of the practice of technical arts involving chemical processes comes from Ancient Egypt. As far back as 3000 B.C., copper, gold, silver, lead, iron and tin were well known, and glass-making, dyeing and soap-making were common industries. These were controlled by the State and by the priests, the artisans who carried out the processes were frequently convicts or slaves. Greece and Rome made little contribution to the advance of industrial chemistry, but to Greece is due the first step in the development of chemical theory.

The celebrated philosopher Aristotle (384-322 B.C.) amplified and re-stated an older theory of the constitution of matter, in

which he asserts that the universe is composed of one primal material which assumes various forms. The simplest of these are the **Four Elements**, Fire, Air, Water and Earth, with which are associated the qualities of Heat, Cold, Wetness and Dryness. Of these qualities each element possesses two. Fire is hot and dry, Air is hot and wet, Water is cold and wet, and Earth is cold and dry. He also held that each element could be transformed into any other. Aristotle was the first to insist upon the importance of experiment and observation as the basis of all theory. This part of his teaching was forgotten, but his erroneous theories of the constitution of matter persisted, and hindered the progress of scientific Chemistry for 2000 years.

The earliest Egyptian writings upon Chemistry date from the third century B.C. and contain descriptions of chemical apparatus and chemical substances, mixed up with accounts of visions, supernatural occurrences and occult speculations. In succeeding centuries chemical treatises depart farther and farther from the consideration of experimental facts and become more and more wildly speculative, magical and incomprehensible. Out of Aristotle's theory that each of the four elements could be transformed into any of the others, grew the idea of the transmutation of the base metals into gold, which occupied the minds of chemists for ten centuries. The transmutation of metals became known as **Alchemy**, a word derived from the Arabic *al* meaning 'the', and *chemi* the old name for Egypt, and its professors were called **Alchemists**.

The Alchemists. One of the most famous of these was Jabir or Geber, born in Arabia, 722 A.D. He, like others of his time, dabbled in magic and mystery, but laid great stress upon the importance of experiment, and made considerable additions to chemical knowledge. To him is due the theory that all metals are composed of sulphur and mercury. If these are perfectly pure and mixed in the proper proportions, the result is the perfect metal, gold. If impure and mixed in other proportions, silver, copper, tin, lead and iron are obtained. Hence, as the base metals consist of the same two constituents as gold, they should be convertible into gold by suitable treatment. Geber was a man of learning and a brilliant chemist. He wrote many books which shew that he was familiar with such processes as reduction, calcination, solution and crystalli-

sation. He discovered nitric acid and invented methods of dyeing, making steel, ink, varnish, etc.

In the centuries following, Arabia and afterwards France, Germany, Spain and Britain produced many distinguished alchemists, some of them physicians as well. If they did not add much to scientific thought, they at least discovered and prepared a large number of chemical substances. Some outstanding names are: in Arabia, Razi (866-925 A.D.), and Avicenna (980-1036); in Germany, Albertus Magnus (1193-1282); in England, Roger Bacon (1214-1292).

The Philosopher's Stone. The period embracing the fourteenth, fifteenth and sixteenth centuries was the hey-day of the alchemist. The Church looked upon alchemy with such a friendly eye, that it came to be regarded almost as a form of religion. Popes and Bishops occasionally practised it, and many monasteries had their chemical laboratories. The great object of research during this period was the Philosopher's Stone. Many alchemists claimed to have seen it; one describes it as of the colour of the wild poppy with the smell of heated sea salt, another says it is transparent and brittle and coloured like a ruby, a third asserts that it may be of any colour. The most extravagant claims were made for this entirely mythical object; for example, that one part of it will transform a million parts of base metal into gold. It was also supposed to have the power of curing disease and conferring the gift of eternal youth. To live for ever, all that was necessary was to take one grain in wine in a silver cup after midnight, the dose to be repeated each month. A solution of the philosopher's stone thus became **The Elixir of Life**. Alchemists also sought for a universal solvent which they called the **Alcahest**. Some of these men were of course honest seekers after truth, but many were frauds and imposters, and as time went on their trickery was exposed. Laws were made against them, and though they died hard, the growing light of knowledge finally dissipated the superstitions of the Middle Ages. James Price, sometimes known as the last of the alchemists, professed in 1728 to have discovered the philosopher's stone, but on the day when he was to have given a demonstration before the Royal Society, he committed suicide. Even in our own time, in the year 1932, an individual claimed to have the secret of transmutation and seems to have deceived many who ought to have known better.

Our modern knowledge of atomic structure, and the success of attempts to break down heavy atoms into lighter ones have made transmutation a possibility, but the tremendous expenditure of energy required far exceeds in cost, at present, the value of any gold which might be obtained.

Iatro-Chemistry. The sixteenth and seventeenth centuries produced a school of chemists who were also physicians and taught that the main object of Chemistry is not to make gold but to heal disease. These were known as the Iatro-chemists or medical chemists, and through their efforts Chemistry became established as an important part of medical education, and began to be taught in medical schools and colleges. The necessity for pure drugs led to the careful purification of chemical substances, and thus paved the way for the great developments in pure Chemistry which began in the latter half of the seventeenth century. One of the pioneers of this school was the alchemist and physician, Paracelsus (1493-1541). Born in Switzerland, he was a man of extraordinary ability, but coarse, passionate and drunken in behaviour. During his short lifetime he wrought many wonderful cures, wrote a number of books and waged continual warfare against his professional brethren, whom he regarded as quacks and charlatans. Van Helmont (1577-1664) was perhaps the greatest of the iatro-chemists. He did not accept Aristotle's four elements, but revived an ancient Greek theory that water is the true principle of all things. As proof of this he performed the following experiment. He dried 200 pounds of earth in an oven, put it into an earthen pot, and planted in it a willow weighing 5 pounds. The tree was regularly watered and after five years it had increased in weight 164 pounds, while the earth after drying had lost only 2 ounces in weight. Hence, 164 pounds of wood, leaves and roots appeared to have been produced from water alone. Only after the lapse of a century was it shewn from the observations of Priestley and others, that carbon dioxide as well as water was the source of the increase of weight. Van Helmont made many experiments with gases, but had great difficulty in collecting them, as the pneumatic trough had not then been invented. He first used the term Gas and discovered carbon dioxide, which he called 'gas silvestre,' and shewed that it was produced from limestone and formed during the processes of fermentation and combustion.

By the middle of the seventeenth century, hydrochloric, nitric and sulphuric acids had become ordinary commercial products. A large number of inorganic salts and metallic oxides were in common use. The knowledge of practical experimental science had enormously increased and the age of modern scientific Chemistry was beginning to dawn.

Robert Boyle (1627-91). Although up to this time the four-element theory of Aristotle had held almost undisputed sway, chemists were beginning to realise that it was quite inadequate to explain the great mass of experimental fact which had gradually been accumulated by scientific workers. Its death-blow was administered by the Hon. Robert Boyle, born in Ireland in 1627. He is best known to students of Chemistry as the author of Boyle's Law, relating to the behaviour of gases under pressure, but his scientific writings cover a wide range of subjects. Boyle has rightly been called the 'Father of Modern Chemistry,' as it was he who really made it an independent science, and freed it from philosophy and mysticism. He insisted that scientific facts should be explained in clear and simple language. In 1661 he published an epoch-making book, *The Sceptical Chemist*, in which he rejects the theory of the four elements, defines an element as a substance which has not been further subdivided, and draws a distinction between compounds and mixtures. Boyle, however, was ahead of his time, and the far-reaching importance of his work was not recognised until many years later.

The next two centuries were extremely fruitful in chemical discovery. Some of the great names of this period, whose work will be discussed in its proper connection, are : John Mayow (1643-78), George Ernest Stahl (1660-1734), Joseph Black (1728-99), Henry Cavendish (1731-1810), Carl Wilhelm Scheele (1742-86), Joseph Priestley (1733-1804), Antoine Laurent Lavoisier (1743-94), and John Dalton (1766-1844).

CHAPTER II

ANALYSIS AND SYNTHESIS. PHYSICAL AND CHEMICAL CHANGE. MIXTURES AND COMPOUNDS

THE world in which we live is composed of many different kinds of material, from which, assisted by the sun and the atmosphere, we have to obtain all the things which are necessary for the support of our lives. In ancient times little was known about these kinds of material; the alchemists, as we have seen, classified them into four elements, earth, water, air and fire. As human knowledge increased, this method of classification was discarded, for it was discovered that earth, water and air could be divided into simpler substances, and that fire was a form of energy.

Analysis and Synthesis. Men have always been curious about the composition of things, they have continually been trying, like children, to pull them apart to see what they are made of. This process of pulling apart, or **Decomposition**, is known as **Analysis**, and the opposite process of putting together or **Combination** is known as **Synthesis**. The study of such processes is called **Chemistry**.

The word **Chemistry** is supposed to be derived from *chemi* meaning the 'black land,' the ancient name for Egypt where the art was, as far as we know, first practised and was known as 'the Egyptian art.'

Physical and Chemical Change. The changes which material or **Matter** undergoes may be divided into two classes, **Physical Changes** and **Chemical Changes**. The term **Matter** is defined as anything which has weight and occupies space, and may be of three kinds, solid, liquid or gaseous. Solids and liquids in bulk, we can see and handle; a colourless gas such as air we cannot see, but we can feel and measure its pressure or weight and thus conclude that it is **Matter**.

Examples of Physical Change. Two of the commonest physi-

cal changes are those which water undergoes when it is cooled or heated. When cooled to a low temperature, the liquid water becomes solid ice; when heated, it is transformed into steam, a gas or vapour. Again, we may fell a tree, saw it into boards, and make these into articles of furniture which bear no resemblance to the original tree; this also is a physical change. These changes are, however, only changes of form or state, ice and steam are merely water in the solid or gaseous state, the furniture is the same material as the tree. A physical change may therefore be defined as a change of form or state without any change of composition. A chemical change goes much deeper, it may involve a change of form or state, but also includes a change of composition, resulting in a totally different kind of matter.

Examples of Chemical Change

EXPT.—Heat a piece of magnesium ribbon in the gas flame, it takes fire and burns to a white powder. The magnesium has united with the oxygen of the air to form magnesium oxide, a new substance.

EXPT.—Heat some red mercuric oxide in a test tube, it gradually turns black, a physical change. On heating more strongly silvery globules of mercury become visible coating the inside of the tube, and a gas is given off which causes a glowing wood splinter inserted in the tube to burst into flame. The mercuric oxide has been split up or decomposed into its two constituents mercury and oxygen, a chemical change.

Conservation of Matter. If a piece of magnesium ribbon be weighed and burned, the white substance produced will be found to weigh more than the original metal. To one unacquainted with the composition and properties of air, it would seem that this extra weight had been produced from nothing, that it had been created. Can matter be destroyed or created? Thousands of experiments have been made to answer this question, and they all go to prove that matter can neither be created nor destroyed by chemical processes. Recent researches in radioactivity, however, indicate that matter can be annihilated or transformed into energy, and that conversely energy can be transformed into matter, in radioactive processes. But as far as the work of the chemist is concerned, matter is indestructible and increatable, and this truth is embodied in the Law of the Conservation of Matter.

Chemical laws have been established from the results of experiment, and we can also by experiment satisfy ourselves as to their truth. In order to carry out experiments quantitatively, that is, by accurate measurement, we generally have to use that indispensable tool, the **Chemical Balance**, and the student should at the outset become familiar with its use.

The Balance. This is a very delicate and expensive piece of apparatus and should always be used with the greatest care. It consists of a beam carrying a steel or agate knife edge which rests upon an agate plane. From each end of the beam a scale-pan is suspended by a metal stirrup also resting on a knife edge. When the balance is not in use, the beam rests upon supports. To the centre of the beam is attached a metal pointer the lower end of which moves across a graduated scale. By means of screws at either end of the beam the balance can be adjusted so as to bring the pointer to rest at the centre of the scale. The weights used by chemists are those of the metric system, of which the gram is the unit. The weights from one gram upwards are usually made of brass, the smaller weights from 0.5 down to 0.01 gram are of platinum, aluminium or nickel. The beam is commonly graduated into ten equal divisions on each side of the centre, and each of these again into tenths. A bent piece of brass or aluminium known as a 'rider,' and weighing one centigram, bestrides the beam and can be moved from one position to another. Weighings from 0.009 to 0.0001 gram can be made by means of the rider, one large division being equal to the addition of 0.001 gram to the scale and $\frac{1}{10}$ equal to 0.0001 gram.

The following rules should be observed when using the balance.

1. The substance to be weighed is always placed in the left-hand pan, and the weights added by means of a forceps to the right.

2. No chemical substance should be placed upon the bare pans, a watch glass or weighing bottle must always be used.

3. When lifting or lowering the beam by means of the lever or milled-edge disc always do so slowly and gently, do not jerk the beam up and down as this injures the balance

4. Never place anything on the pans when the beam is swinging.

Let us now test the truth of the Law of the Conservation of Matter.

EXPT.—Put some clean iron filings moistened with water into a flask. Cork the flask tightly and weigh. Allow it to stand for a day or two and weigh again. Although the iron has rusted, a chemical change, the total weight is unaltered.

EXPT.—Take a dry round-bottomed flask and place a layer of dry sand in it. Cut off a small piece of phosphorus, dry it between filter papers and drop it on the sand.

Note that phosphorus must be cut under water, it should on no account be handled with the fingers, as it may take fire and cause severe burns.

Close the flask with a tightly fitting rubber stopper, and weigh. Then clamp it on a retort-stand in the fume cupboard in case the flask bursts. Heat gently till the phosphorus ignites, then leave it to burn out. When cool weigh the flask again; the weight should be unchanged.

EXPT.—Put into a flask some dilute sulphuric acid. Take a small test tube containing a little barium chloride solution and place it in the flask with the mouth of the tube just above the surface of the acid. Cork tightly and balance the flask exactly with weights. Remove from the balance and shake till the acid and barium chloride mix. A chemical reaction has taken place. Place the flask again on the pan; it should still balance exactly.

Mixtures and Compounds. If we examine different kinds of material, we find that many of them are not of the same composition throughout, that is, they are **Heterogeneous**. Substances which are the same throughout are said to be **Homogeneous**, and it is to the latter class that the word substance is usually applied in chemistry. Homely examples of these two classes are, respectively, a plum pudding and a jelly. A heterogeneous material or **Mixture** can be separated into its component parts by mechanical means, while a homogeneous substance or **Compound** requires chemical methods.

EXPT.—Take 5 parts of clean iron filings, and 3 parts of flowers of sulphur by weight. Mix these thoroughly on a sheet of paper. Examine the mixture with a magnifying lens. You will find that both constituents are visible side by side, and using a needle point, you can separate them from each other. Draw a bar magnet across the mixture; the iron only is attracted, and clings to the magnet, carrying with it however a little adhering sulphur.

A more perfect separation can be made by the method of Solution (Chap. III).

EXPT.—Place a small quantity of the mixture in a test tube, add some carbon disulphide and shake. Prepare a filter paper by doubling it twice to form a quarter circle, open it out into a cone and press the cone into a glass filter funnel, taking care that it fits closely. Set the funnel on a filter stand and place underneath it a porcelain basin. Pour off the liquid in the test tube into the filter (see that it does not rise above the edge of the paper), and repeat the treatment with carbon disulphide once or twice, filtering each time, until the iron appears to be free from sulphur. Let the liquid in the basin stand for an hour or two to evaporate. A crystalline residue (see next chapter) of sulphur will remain, which may be examined with a lens.

Note that the vapour of carbon disulphide is very inflammable, so that it should not be brought near a gas flame.

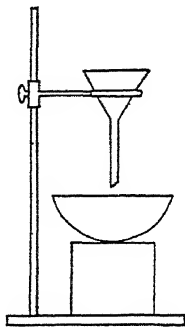


FIG. 1.

Making a Compound. **EXPT.**—Place in a hard glass test tube another portion of the mixture of iron filings and sulphur. Heat it in the flame of a Bunsen burner, and withdraw the tube from the flame immediately the mixture begins to glow. Note that it continues to glow still more brightly. The heat of the flame is necessary to start the chemical change or reaction, but once started, the heat given out is sufficient to carry it to completion.

In a chemical change or 'reaction' (a term usually employed instead of chemical change), heat may either be given out or absorbed. When there is an evolution of heat the reaction is termed **Exothermic**; when heat is absorbed, it is called **Endothermic**. In the latter case the application of heat is necessary until the reaction is completed. Exothermic compounds, that is, compounds formed with evolution of heat, are invariably more stable, they are more difficult to decompose than endothermic compounds.

EXPT.—Continued. Having allowed the substance in the test tube to cool, turn it out on a sheet of paper. It is a dark grey mass, practically non-magnetic, insoluble in carbon disulphide, and on examination with a lens does not shew the two constituents. It is a compound of iron and sulphur known as **Sulphide of Iron**, or more correctly, **Ferrous Sulphide**.

The composition of this substance does not vary, it always contains iron and sulphur in the proportion of 56 parts to 32 by weight, but the iron and sulphur are so intimately united that they have lost their individual properties and do not respond to tests. This constancy of composition is a property of all chemical compounds; a compound may be made in several different ways, but in each case the percentage composition is the same.

EXPT.—Weigh a porcelain crucible. Then weigh in the crucible about a quarter of a gram of magnesium ribbon. Cover with a lid and heat till the magnesium has burned, raising the lid occasionally to admit air. Allow to cool and weigh again. Subtract weight of crucible to get the weight of oxide.

Note that in heating magnesium in air a little magnesium nitride is formed, which gives a lower result. If a supply of oxygen is available it is better to heat the magnesium in oxygen, which gives the pure oxide.

EXPT.—Weigh or counterpoise a dry test tube provided with a plug of glass wool. Place in it the same quantity of magnesium ribbon and weigh. Keeping the tube in a sloping position, add sufficient dilute nitric acid to dissolve the magnesium. Clamp it in a retort stand and heat carefully with the Bunsen till dry, shaking occasionally; oxide of magnesium is left.

We have thus made magnesium oxide by two different methods, and if the experiments have been carefully performed the weights of magnesium oxide should agree. This shews that the composition of magnesium oxide does not vary when differently prepared, and the same is true of all chemical compounds.

Measurement of Liquids. It is convenient to have a general idea of the capacity of various vessels such as flasks, beakers and test tubes. This is usually stated in cubic centimetres or c.c. One c.c. of water weighs one gram, and there are 1000 c.c. in one litre.

EXPT.—Pour into a test tube from a measuring cylinder successive quantities of 5 c.c., 10 c.c. and 15 c.c. of water, and make a small scratch with a file to mark these levels. Fill a test tube and make a note of its capacity in c.c. Next take three or four beakers and measure their capacity by filling with water from the cylinder. Perform the same operation with flasks of different

sizes. Take a note of the capacity of all these vessels. It will be easy afterwards to measure roughly any required quantity of liquid without the necessity of using a graduated cylinder.

Additional Experiments

EXPT.—To separate gunpowder into its constituents, nitre, sulphur and carbon.

EXPT.—To make cuprous sulphide by heating copper and sulphur together.

EXPT.—To make lead iodide. Melt a little lead in a test tube. Add iodine. Remove excess of iodine by heating and sublimation. Plunge hot tube into cold water. Break up the substance and boil it with a little water. Filter hot, and observe the crystallisation of lead iodide on cooling.

QUESTIONS

1. Explain what you understand by (a) chemical change, (b) physical change. Give illustrations of each.
2. Define the terms 'decomposition,' 'combination,' 'analysis,' and 'synthesis.'
3. Explain the difference between a mixture and a compound. Give an account of some methods of separating the constituents of a mixture.
4. Describe fully an experiment illustrating each of the following: (a) making a compound from two elements, (b) decomposing a compound into its elements.
5. What do you understand by the expression 'the Law of the conservation of matter'? Give details of two experiments designed to test the truth of this Law.

CHAPTER III

SOLUTIONS. SOLUBILITY CURVES. CRYSTALLISATION

THE method of solution is extensively used in Chemistry for separating substances which are soluble in some particular liquid, from those which are insoluble.

A Solution may be defined as a *homogeneous mixture* of a solid, a liquid, or a gas, with a liquid. The substance which is dissolved is known as the **Solute**, the liquid which dissolves it is the **Solvent**, and the mixture of both is the **Solution**. The most common solvent is water. Substances which are insoluble in water may be dissolved by other solvents, *e.g.* carbon disulphide dissolves sulphur, phosphorus and rubber; benzene and petrol dissolve oil and grease, and are used for cleaning soiled clothes.

Solubility. **EXPT.**—To half a test tube full of water, add powdered common salt (sodium chloride) in small quantities at a time, shaking well after each addition. After a certain quantity has been added, it will be found that any further addition of salt remains undissolved. The liquid is then said to be **saturated** with salt, and is called a **saturated solution**. The liquid and the solid, if there is no alteration of temperature, remain in contact without any change, and are said to be in **equilibrium**.

Solubility generally, but not always, increases with rise of temperature. The solubility of potassium nitrate, for example, increases rapidly, while sodium chloride is almost as soluble in cold water as in hot; a few salts, indeed, become less soluble at high temperatures.

That weight of a substance which will dissolve in 100 c.c. of water at any definite temperature, to make a saturated solution, is known as the **Solubility** of the substance in water at that temperature. The strength or **Concentration** of a solution

depends upon the relative quantity of solute which it contains. If the quantity dissolved is small compared with its solubility it is called a weak or Dilute solution; if it is large, approaching saturation, it is called a strong or Concentrated solution. The solubility of a substance can be determined by the following method.

EXPT.—Half fill a 100-300 c.c. beaker with water. Place a thermometer in it, and stand it on a piece of wire gauze supported by a tripod. Warm gently with a Bunsen flame until a temperature of about 30°C . is reached. Add potassium nitrate, stirring continuously, and keeping the temperature as close to 30°C . as possible, until a quantity of the salt remains undissolved; this gives a saturated solution. Pour out into a weighed porcelain basin or draw off with a pipette, about a third of the solution, taking care that no solid is drawn off, and note the exact temperature. Allow the basin to cool and weigh basin and solution. Then evaporate to dryness and weigh the basin and residue. From these results the weight of substance which is dissolved by 100 c.c. of water at the observed temperature can be calculated, taking the weight of one c.c. of water as one gram. Avoid overheating on evaporation.

Half a dozen measurements of solubility may be made at different temperatures, and a Solubility Curve plotted, where the ordinates (verticals) represent solubilities, and the abscissae (horizontals) represent temperatures.

The accompanying diagram shews the solubility curves of potassium nitrate, sodium chloride and sodium sulphate. Observe that the solubility of potassium nitrate increases very rapidly with rise of temperature, that of sodium chloride increases slowly, while the solubility of sodium sulphate increases

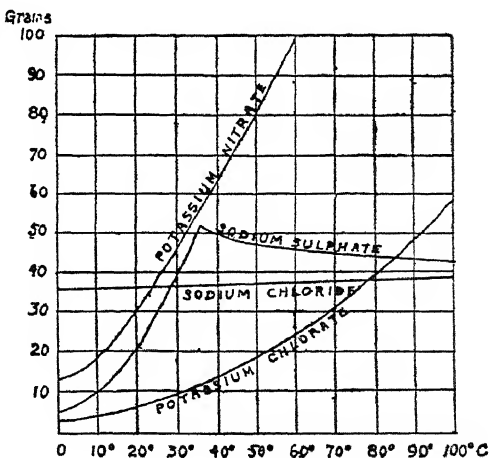


FIG 2 —Solubility Curves

up to a temperature of about 35°C ., and then begins to decrease.

EXPT.—Find the solubilities of potassium chloride and potassium chlorate at 20° , 40° , 60° , and 80°C ., and draw the solubility curves.

Under certain circumstances a solvent may retain in solution more of the solute than the solubility quantity. It is then called a Supersaturated solution.

EXPT.—Take a wide test tube half filled with crystals of sodium thiosulphate (photographers' hypo), and stand it in a beaker of boiling water. The salt melts, and forms a very strong solution. Remove the tube from the beaker and stop its mouth with a plug of cotton wool. If it is allowed to cool undisturbed it will remain liquid, forming a supersaturated solution. When cool, remove the plug and drop a crystal of the salt into the tube. The liquid seems to solidify rapidly, and a thermometer introduced into the mass shews a rise of temperature.

The word Salt in the last paragraph does not refer to sodium chloride or common salt only, but to a large class of substances, of which sodium chloride and sodium thiosulphate are examples. An unsaturated solution, a saturated solution, and a supersaturated solution can be distinguished by adding to the liquid a small quantity of the solute. In the first case the added solute dissolves wholly or partially, in the second case there is no change, in the third case additional solid separates out from the liquid.

Crystallisation. When a hot saturated solution of a salt in water is allowed to cool it generally deposits crystals.

EXPT.—Make a concentrated solution of copper sulphate by adding the powdered salt to half a beaker of hot water, till no more is dissolved. Pour the liquid into a basin, allow to cool and examine the crystals.

The solubility curve shews that, in the case of a saturated solution of a salt whose solubility increases with rise of temperature, if the temperature be lowered, the whole of the solute cannot be kept in solution and the excess crystallises out. Every crystal has a definite geometrical shape, though in the mass this is not always obvious, as adjoining crystals may

interfere with each other's regular growth. A crystal is built up by the addition of crystal units, which are added as regularly as bricks by a bricklayer. It has plane faces and the angles between these faces are always the same for each crystalline substance. Not all substances are crystalline; non-crystalline substances are said to be **Amorphous**, that is 'shapeless,' but the essential difference between the two classes is that the former have a definite internal structure which is not found in the latter, the difference between a brick wall and one built of concrete. Glass and resin are two examples of amorphous substances, when melted and cooled they do not crystallise; it is not therefore strictly correct to call glass crystal.

Water of Crystallisation. Some crystals when they form from a solution combine within themselves a definite amount of water, known as water of crystallisation. On heating they generally lose this water and fall into powder.

Expt.—Heat a crystal or two of copper sulphate in a test tube. Moisture condenses on the cool part of the tube, the substance finally turns white and is then known as **Anhydrous** copper sulphate. When moistened it takes up water and becomes blue again; this reaction is sometimes used as a test for water.

Some crystals lose their water of crystallisation at ordinary temperatures. This change is known as **Efflorescence**.

Expt.—Expose a large crystal of washing soda to the air, note that it slowly loses water, becomes opaque, and finally falls into powder.

Certain crystalline substances, on the other hand, have an attraction for water. They absorb water from the air and dissolve in the water thus attracted. This property is known as **Deliquescence**.

Expt.—Expose some potassium carbonate to the air, and observe any change that may take place.

Some substances absorb water from the air, but not sufficient to dissolve them. They are said to be **Hygroscopic**. All crystals do not contain water of crystallisation.

Expt.—Weigh some dry sodium chloride in a crucible and heat. Cool and re-weigh, there is no loss of weight. Repeat the experiment with potassium sulphate.

Fractional Crystallisation. We have seen that 100 c.c. of water cannot dissolve more than a certain definite weight of a salt at any particular temperature. This weight is different for each salt, and is known as its solubility at that temperature. Consequently, if a hot saturated solution of a salt is allowed to cool, it deposits crystals continuously. The solubility decreases with falling temperature and the excess weight which cannot be kept in solution must crystallise out. We have also seen that the solubility of some salts increases much more rapidly with rise of temperature than that of others. On these two considerations is based a method for the separation of soluble crystalline substances called Fractional Crystallisation.

Let us consider two salts, the solubility of one increasing rapidly with rise of temperature, and that of the other slowly, potassium nitrate and sodium chloride. Make up a mixture of equal parts of these and dissolve 100 grams of it in 50 grams of boiling water. The solubility curve diagram shews that 100 grams of water at 100°C . will dissolve more than 130 grams (actually about 230) of potassium nitrate, so that 50 grams of water will easily dissolve 50 grams of the salt. The sodium chloride curve shews that 100 grams of water at 100°C . dissolves about 38 grams, so that 50 grams of the nitrate and 19 grams of the chloride go into solution. Pour off the liquid and allow to cool down to room temperature, say 15°C . Referring again to the curves, 50 grams of water dissolve 13 grams of the nitrate and 18 grams of the chloride at 15°C ., hence 37 grams of potassium nitrate and about 1 gram of sodium chloride have crystallised out. Pour off the liquid again and wash the crystals with ice-cold water. The remaining sodium chloride is dissolved, as shewn by the curves it is three times more soluble than potassium nitrate at 0°C ., and pure potassium nitrate is left.

Crystal Form. Haüy's Law (1801) states that every crystalline substance has a definite crystalline form characteristic of that substance. A crystal is bounded by plane surfaces which are called faces, and though the shape of the faces may vary, the angles between corresponding faces are always the same and are characteristic of the particular substance. Thus the final test of the crystalline form of a substance is not the size or shape of its faces, but the angles at which the faces meet.

Crystals are classified with reference to certain imaginary lines supposed to be drawn through the crystal and called its axes. These axes intersect within the crystal, and according to their relative length and inclination to one another, all crystals are divided into six systems: the regular, tetragonal, hexagonal, rhombic, monoclinic and triclinic systems.

Crystal Systems

1. **Regular.** In this system there are three axes which are all equal and all at right angles to one another. Common forms of this system are the cube and octahedron.

Examples: Common salt, cube. Alum, Octahedron.

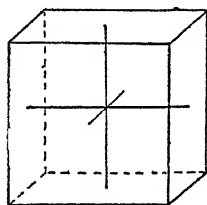


FIG. 3.

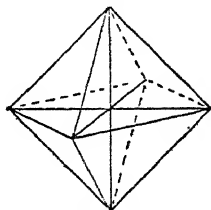


FIG. 4.

2. **Tetragonal.** The axes are all at right angles to one another, two are equal in length, the third may be longer or shorter. The latter is the primary axis, the other two are secondary axes.

Examples: Tin stone or cassiterite; potassium ferrocyanide.

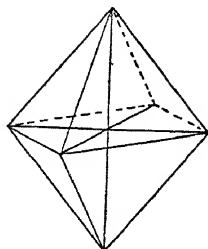


FIG. 5.

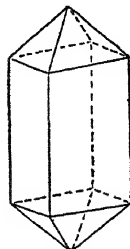


FIG. 6.

3. **Hexagonal.** This system is distinguished from all the others by the fact that it possesses four axes. Three secondary axes are equal in length and lie in the same plane. They intersect each other at an angle of 60° and are all at right angles to the fourth or primary axis which is of different length.

Examples : Calcite ; quartz ; sodium nitrate.

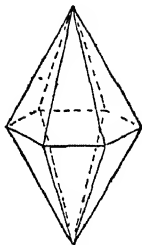


FIG 7.

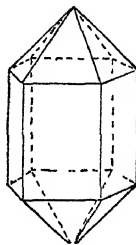


FIG 8

4. **Rhombic.** The axes of this system are three in number, all of different lengths, but all at right angles to one another.

Examples : Sulphur ; potassium nitrate.

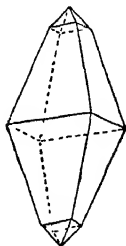


FIG 9.

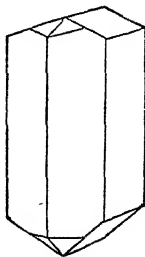


FIG. 10.

5. **Monoclinic.** All three axes are of unequal length. One of the secondary axes is perpendicular to the primary axis, and the other cuts it at an oblique angle.

Examples : Sulphur ; sodium carbonate.

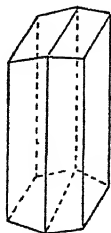


FIG. 11.

6. Triclinic. This is the most unsymmetrical system. All the axes are unequal and are inclined to one another at an oblique angle.

Examples : Copper sulphate ; potassium dichromate.

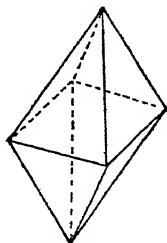


FIG. 12.

Polymorphism. Crystals of the same substance may have different forms when developed under different conditions.

Examples : Sulphur ; sodium chloride ; alum. A substance which crystallises in two different forms is said to be dimorphous, and one which may have three different forms is called trimorphous.

Isomorphism. It was observed by Mitscherlich (1819) that substances which are closely related in chemical structure frequently crystallise in the same system with the same or nearly the same angles, and that a crystal of one such substance will continue to grow when placed in a solution of another. To this he gave the name *Isomorphism*, and such substances are said to be *Isomorphous* or of similar shape.

Examples : Potassium permanganate and potassium perchlorate crystallise in the rhombic system and form mixed crystals. Another pair is potassium iodide and ammonium iodide. The alums are also good examples of isomorphism.

QUESTIONS

1. Explain the terms 'solution,' 'solute,' and 'solvent.' Describe the method of constructing the solubility curve of a salt.

2. What is a saturated solution ? Describe carefully all you would do (a) to prepare aqueous solutions of common salt saturated at 0°C . and 100°C . respectively, and (b) to ascertain accurately by means of these solutions the solubility of salt in water at the two temperatures given. (London Matric.)

3. How may an unsaturated solution, a saturated solution, and a supersaturated solution be distinguished from one another ?

4. Write a short account of the phenomenon of crystallisation. What is the essential difference between crystalline and amorphous substances ?

5. Define the terms 'efflorescent,' 'deliquescent,' and 'hygroscopic,' and mention one substance belonging to each of these classes.

6. What is the final test of the crystalline form of a substance ? Describe the method of classifying crystals, and name the six crystalline systems. What is meant by the words 'polymorphous' and 'isomorphous' applied to crystals ?

CHAPTER IV

THE ATMOSPHERE

THE air which we breathe and which is necessary for the support of our lives completely surrounds the earth like the skin of an orange. We do not know the exact thickness of this skin or envelope, but it cannot be much more than a hundred miles. The atmosphere becomes rarer and lighter as the distance from the earth's surface increases, and above five or six miles becomes too rare to support human life. An aeroplane has ascended to eight miles, and a balloon to thirteen miles, but the occupants had to assist breathing by inhaling oxygen, and their clothes had to be electrically heated on account of the intense cold.

As air has weight, a column 100 miles high must exercise considerable pressure. This pressure can be measured and is found to be roughly 15 pounds per square inch. This is known as a pressure of One Atmosphere.

As far back as 100 B.C. the ancient philosophers had made experiments shewing that air is a material substance. Later, it was observed that some substances, in contact with the atmosphere, undergo mysterious changes. A piece of bright iron exposed to air and moisture becomes in time completely changed into a brown substance called rust, which is heavier than the original iron. Most metals when heated in air are converted into a substance different in appearance and properties, and heavier than the original metal. The first light upon the subject was thrown by some experiments published by John Mayow in 1674. He found that if a candle were burned in a bell jar of air standing in water, the water rose in the jar, shewing that the amount of air had been diminished, and after a time the candle was extinguished. He also shewed that a mouse could not live in the air which was left. A century

later, Scheele, a Swedish chemist, came to the conclusion that the air is composed of two gases, one of which he called Foul Air and the other Fire Air, now known as nitrogen and oxygen respectively.

EXPT.—Wrap up some clean iron filings in a piece of gauze, moisten with water and attach the bag to the end of a glass rod. Place the rod and bag as shewn in the illustration in a jar of air standing in an inch of water. Allow to stand for a day or two, observing that the water gradually rises. When it has ceased to rise, cover the mouth of the jar under water with a glass plate. Remove and invert the jar and measure the volume of water which it contains. This is the volume of gas removed by the iron filings, and should be almost $\frac{1}{5}$ of the volume of the original air or volume of the cylinder. Test the remaining gas with a lighted taper.

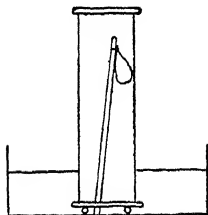


FIG 13.

EXPT.—Obtain a stoppered and graduated bell jar, or graduate one for yourself by pouring into it successively 6 or 7 equal quantities of water, marking each level with a piece of gummed paper; the seventh addition should almost fill the jar. Remove the one hole rubber stopper (which must fit tightly), and place the jar upon a glass rod triangle in a trough of water. Get a large piece of cork and make a hole in the centre of it to accommodate a porcelain crucible. Cut off and dry (using the precautions already given) a piece of phosphorus about the size of a large pea. Transfer this to the crucible and float cork and crucible on the water inside the bell jar. Suppose that the jar has been graduated into 7 divisions, then arrange the level of the water so that it stands at graduation mark 5. Push a closely fitting piece of glass rod (long enough to reach the phosphorus) through the hole in the stopper. Vaseline its upper part so that it may slide easily. Then heat the end of the rod, insert the stopper and push the rod down to ignite the phosphorus. The level of the water in the jar first falls as the air expands from the heat of combustion. Afterwards it rises again, and should finally remain steady about graduation 4, showing that $\frac{1}{5}$ of the air has disappeared. Test the remaining gas with a lighted taper.

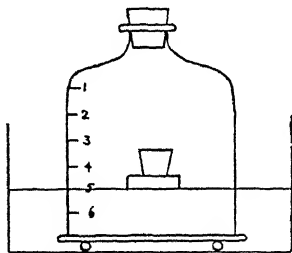


FIG 14

To ensure the success of the experiment there should be a little

phosphorus left unburnt after it is over; this can be tested with a hot glass rod. The water level in the jar must be high enough to prevent any escape of air during the first expansion, and the jar should be cooled with a stream of water.

Composition of Air. These experiments shew us that air contains $\frac{1}{5}$ of its volume of a gas which unites with iron and supports the combustion of phosphorus. This gas is Scheele's 'fire air' or **Oxygen**. The remaining $\frac{4}{5}$ is a gas known as **Nitrogen**, which we shall study later. We have, however, learnt two things about it, that it is not inflammable and does not support combustion. The proportions of oxygen and nitrogen vary slightly in different places; the average composition is taken as 21% of oxygen and 79% of nitrogen by volume. But as oxygen is rather denser than nitrogen, the percentages by weight are 23 and 77. The atmosphere also contains small quantities of other gases. Carbon dioxide is present to the extent of about 3 parts in 10,000 by volume. Water vapour or moisture varies in quantity according to the temperature, and may average 1%. Nitrogen, obtained from air by methods similar to those given above, contains 0.75% of a gas known as **Argon**. This gas is one of a family called the 'inert gases,' because they are chemically very inactive, forming no compounds. Their names are: Helium, meaning 'sun'; Neon, 'new'; Argon, 'inert'; Krypton, 'hidden'; and Xenon, 'stranger.' They are all present in the atmosphere, argon to the extent of nearly 1%, the others in very minute quantities. While investigating the density of nitrogen, Lord Rayleigh (1893) found that the density of atmospheric nitrogen is greater than that of nitrogen obtained from nitrogen compounds, from which he inferred that the nitrogen of the air contained a small quantity of an unknown and denser gas. The gas was isolated by W. Ramsay in 1894, and was named Argon. Helium had previously been detected in the sun by means of the spectro-scope, and was afterwards extracted from certain minerals by Ramsay. Helium is light and non-inflammable and is used for filling airships; it is obtained from natural gas in American and Canadian oil fields. A mixture of oxygen and helium is found by divers better for breathing purposes than ordinary air. Neon is used for filling electric light tubes, used in advertising signs; they give out a brilliant coloured light. Neon-filled lamps are also used as fog lamps in some British aerodromes.

Is Air a Mixture or a Compound? All the evidence points, to the conclusion that air is a mixture.

1. We have seen that the proportions of oxygen and nitrogen vary slightly in different localities, but the composition of a pure chemical compound does not vary even in a small degree.

2. The formation of a compound is usually attended by an evolution or absorption of heat, but when we mix oxygen and nitrogen in the proportions in which they are present in air, there is no sign of any heat change, and the mixture behaves in every respect like ordinary air.

3. Nitrogen and oxygen can be obtained from the atmosphere by liquefying air and allowing the nitrogen to evaporate. They can also be separated by the method of solution as oxygen is more soluble than nitrogen. Compounds cannot be decomposed by such methods.

4. The proportions of oxygen and nitrogen do not agree with the requirements of the law of multiple proportions, according to which, if air were a compound, they should be capable of representation by small whole numbers, which is not the case. In addition, the vapour density of air is not what it should be if it were a compound of oxygen and nitrogen.

From these and other considerations, we conclude that air is a mixture, not a compound.

One of the chief functions of nitrogen in the atmosphere is to dilute the oxygen, as oxygen breathed alone would be far too stimulating for ordinary existence. If we lived in an atmosphere of pure oxygen, all our activities would be carried out with such a tremendous expenditure of energy that our bodies would be quickly worn out, and human life would be a short and merry one.

Carbon dioxide and water vapour are not to be regarded as merely impurities in the atmosphere. On the other hand, though small in quantity in proportion to nitrogen and oxygen, they are very essential constituents of air. Carbon dioxide is necessary for plant growth and consequently for the support of animal life, and without water vapour we should have no refreshing rain to clean the atmosphere and fertilise the ground. It is possible also that the inert gases may play their part in Nature's drama, but their rôle has yet to be discovered.

Additional Experiments

EXPT.—To shew that air has weight. Take a round-bottomed flask with a one-hole rubber stopper. Fit into it a 3-inch piece of glass tubing, to the outer end of which attach a piece of rubber tube carrying a clip. Exhaust the flask with an air pump and balance it. Open the clip and note increase of weight.

EXPT.—To shew that air contains carbon dioxide. Bubble air for some time through lime water. It turns milky.

EXPT.—To shew that air contains nitrogen. Burn some magnesium *powder* to get the mixture of oxide and nitride. Moisten with water and hold a piece of moist red litmus paper over it. The ammonia given off blues the paper and the smell can be observed. If reaction does not take place at once, boil the calx with a little water and test the vapour in the same way. Ammonia contains nitrogen and this has come from the air.

QUESTIONS

1. Write a historical account, extending to not more than a page and a half, of 'the chemistry of the air.' (Scot. Leaving Cert.)

2. Wet iron filings are confined with air in a glass tube. Describe all that may be learnt from this experiment.

(London Matric.)

3. Describe carefully an experiment designed to shew that air consists mainly of two gases in the proportion of 1 : 4 by volume. What names did Scheele give to these two gases? What are they now called?

4. Besides the two chief gases of which air is composed it contains other gases in smaller quantity. Name these. What are the 'inert gases'? Tell what you know about their discovery.

5. Is air considered to be a mixture or a compound? Give as many reasons as you know in support of your answer.

6. Nitrogen derived from the air by removal of oxygen has a density of 14.070, whereas pure nitrogen has a density of 14.005. Explain the discrepancy, and write a short historical note on the researches which dealt with it. (Scot. Leaving Cert.)

CHAPTER V

OXYGEN

The Phlogiston Theory. Most metals when heated in air lose their bright metallic appearance and are transformed into a dull powdery substance. Zinc and magnesium burn brilliantly, leaving a white residue. In the seventeenth century the residue left on burning or heating a metal was known as the 'calx' of the metal, and the process was called 'calcination.' We know now that the calx is formed by the union of the metal with the oxygen of the air, but at that time oxygen had not been discovered, and to explain the phenomena of combustion and calcination, Stahl (1660-1734) suggested the Phlogiston theory.

According to this theory, combustible substances such as coal, wood, oil, burn because they are rich in phlogiston. It is regarded as the material of fire and its expulsion from a substance results in flame, light and heat. Thus when metals are heated they lose phlogiston, leaving behind calces. But if lead or zinc calx is heated with coal or charcoal, the metal is again obtained; coal and charcoal give up phlogiston to the zinc or lead and thus restore it to its metallic nature. Further, neither combustion nor breathing is possible in air saturated with phlogiston, so a candle burned in a limited supply of air gives up its phlogiston to the air and is extinguished when the air can take up no more phlogiston. At this time the balance had not become the indispensable instrument it now is in checking chemical reactions, and although many chemists observed that the calx of metal was heavier than the metal itself, although it was supposed to have lost something, they put this aside as incapable of explanation. This theory was universally accepted for about a century.

Joseph Priestley and the discovery of Oxygen. The Swedish

OXYGEN

chemist Scheele, a contemporary of Priestley, had shewn that the atmosphere is composed of two gases. He observed that there is a definite decrease of volume when phosphorus or hydrogen is burned in a limited quantity of air, and that the remaining gas is lighter than the original mixture. He also obtained the gas which we now call oxygen by heating saltpetre, mercuric oxide and other substances, but his results were not published till 1777, after Priestley had announced his great discovery.

In 1774 Joseph Priestley, an English minister and a brilliant scientist, prepared oxygen by heating mercuric oxide, calx of mercury, with a 'burning glass' or convex lens. The substance was confined in a cylinder containing mercury and inverted in a trough of mercury. He collected a quantity of the gas, and found, in his own words, "that a candle burned in this air with a remarkably vigorous flame."

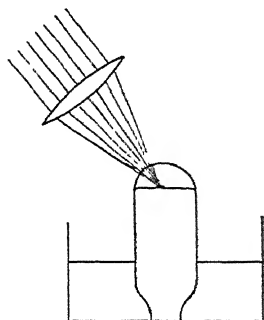


FIG. 15 — Priestley's Experiment

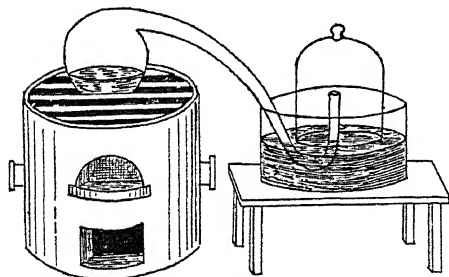


FIG. 16 — Lavoisier's Apparatus.

than the metal itself, and now became convinced that mercury when converted into calx by heating in air combines with the active part of air, which the calx gives off again when more strongly heated. He proved this theory by heating 4 oz. of mercury in a retort which communicated with a bell jar

supporter of the phlogiston theory and called the gas 'dephlogisticated air.' In the same year he announced his discovery to the French chemist Lavoisier, who repeated his experiments and came to the conclusion that the new gas was identical with the constituent of air which supports combustion. Lavoisier had been puzzled by the fact that the calx of a metal weighs more

containing a measured volume of air confined over mercury. The mercury became covered with red particles, red calx of mercury. After heating for twelve days he found that the air in the bell jar had been reduced from 50 cubic inches to 42 inches, and that the weight of red particles produced was 45 grains. The air left behind did not support combustion or respiration. He then took 45 grains of the red substance, heated it in a retort, and collected in a bell jar 8 cubic inches of gas, in which combustible substances burned brilliantly. The volume of gas given off by the calx was thus the same as the volume which had been absorbed by the mercury. This experiment proved the death-blow of the phlogiston theory, as it showed conclusively that metals when heated do not lose phlogiston but combine with the active part of air, which explains their increase of weight. Lavoisier afterwards called the gas **Oxygen** or 'acid former.'

Occurrence. Oxygen is present in the free or uncombined state in the atmosphere to the extent of 21% by volume and 23% by weight. In water it is found combined with hydrogen. It is the most abundant element (a term explained in the next chapter) found in nature. It enters into the composition of animals, plants, and rocks, and forms about 50% by weight of the crust of the earth.

Preparation. Oxygen may be made in the laboratory by the method used by Scheele and Priestley, by heating mercuric oxide.

EXPT.—The apparatus is arranged as shewn in the sketch. A small quantity of the oxide is placed in a hard glass test tube which

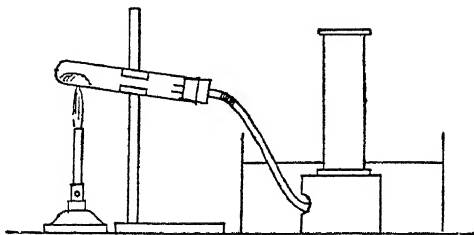


FIG. 17.

is clamped on a retort-stand. The leading tube of glass dips under the water of a **Pneumatic Trough**, in which a wide test tube or

small gas jar is filled with water and inverted over the beehive to collect the gas given off. The tube is strongly heated with a Bunsen flame. Bubbles of gas come over and displace the water in the jar. The first portion collected consists mainly of the air contained in the tube, and may be rejected. The tube is then refilled with water and heating continued till a sufficient quantity of oxygen is obtained. Note that in this and similar experiments if the tube is allowed to cool there may be a danger of the water in the trough being sucked back, in which case the tube will inevitably be broken and the experiment ruined. This should be guarded against by keeping the tube heated, and when the experiment is over the leading tube must be at once disconnected. Now close the collection tube under water with the thumb, or if a jar is used, with a greased glass plate. Remove it from the trough, and holding it mouth upwards, uncover it and quickly insert a splint of cedar wood which has been heated to glowing in the flame of the Bunsen. Observe that the glowing splint bursts into flame, and oxygen is consequently known as a supporter of combustion or burning. This serves as a test for oxygen.

Oxygen may also be prepared by heating potassium chlorate. Mercuric oxide contains 7% of oxygen, while potassium chlorate contains nearly 40% and on heating gives off the gas at a much lower temperature.

EXPT.—Heat some crystals of potassium chlorate in a test tube. They first crackle and fly in pieces, then melt, and finally the liquid bubbles owing to the evolution of oxygen gas. The gas in the tube may be tested with a glowing splinter, or it may be collected over water as in the last experiment.

If potassium chlorate is heated long enough, it loses all its oxygen and is converted into potassium chloride; 245 parts of potassium chlorate give 149 parts of potassium chloride by weight.

EXPT.—To verify these proportions, weigh a porcelain crucible with lid carefully, put into it about one gram of the salt and weigh again; the difference gives the weight of potassium chlorate. Heat gently at first but finally with the full heat of the burner. Having heated the crucible for ten minutes, allow it to become quite cool and weigh. Re-heat for five minutes, cool and weigh again. Continue this process until two successive weighings agree, when it may be taken that all the oxygen has been driven off. Subtract the weight of the empty crucible and lid from the final weight; this gives the quantity of potassium chloride which has been

produced. The proportions of chlorate and chloride should be similar to those given.

There is a still more convenient method of making oxygen, the one which is in general use, as the gas is evolved at a much lower temperature. Potassium chlorate, preferably in the form of coarse crystals, is mixed with a small quantity of manganese dioxide, and the mixture (known sometimes as oxygen mixture) heated as before.

EXPT.—Heat some oxygen mixture in a tube as before and test for the gas. This time heat gently as the oxygen comes off at a low temperature, and the evolution may become too violent if heated strongly.

The manganese dioxide contains 37% of oxygen, but does not give it off at the low temperature used, though it does lose oxygen when strongly heated. It remains unchanged at the close of the experiment, and this may be easily demonstrated by weighing the original quantity added, and dissolving the final mixture of manganese dioxide and potassium chloride in water. The dioxide is insoluble and can be separated by filtration, dried and weighed. The part which it really plays is to help the potassium chlorate to yield up its oxygen at a lower temperature. A substance which helps a chemical reaction to proceed and remains unchanged itself is known as a *Catalyst*. Many such substances are used in the chemical industries, for example, in the manufacture of sulphuric acid and ammonia, and will be referred to in the proper places.

Properties. Oxygen is a colourless, tasteless, and odourless gas. It is rather heavier than air.

EXPT.—To find the weight of a litre of oxygen. Take a half-litre thin glass flask. Dry it carefully by warming over the Bunsen flame, blowing out the moist air with a bellows. Allow the flask to stand until quite cold. Cork it with a tightly fitting rubber stopper and weigh. This gives the weight of the flask and the air contained in it. Then remove the stopper and pass a rapid current of oxygen from a gas-holder or cylinder into the flask until the air is completely displaced. Replace the stopper quickly and weigh again. This gives the weight of flask and contained oxygen. Finally find the volume of the flask by filling it with water, pushing in the stopper to expel excess of water and pouring into a measuring cylinder.

We may take it that 1 c.c. of air weighs 0.00129 gram
Let V represent the volume of the flask in c.c., then

Weight of flask plus air	=	_____	grams.
Weight of air is $V \times 0.00129$	=	_____	grams.
Weight of flask	=	_____	grams.
Weight of flask plus oxygen	=	_____	grams.
Weight of flask	=	_____	grams.
Weight of oxygen	=	<u> x </u>	grams.

$$\text{Weight of a litre of oxygen} = \frac{1000 \times x}{V} \text{ grams.}$$

Oxygen is only slightly soluble in water. It is necessary for the support of both plant and animal life, even fishes require dissolved oxygen in the water. In breathing, oxygen is drawn into the lungs and is absorbed by the blood, which contains a substance called haemoglobin. This unites with oxygen to form oxyhaemoglobin, giving the blood a bright red colour. The blood is pumped by the heart into the numerous arteries and the oxyhaemoglobin readily gives up its oxygen to oxidise the waste products of the body, partly transforming them into carbon dioxide which is breathed out by the lungs. In cases of sickness when the lungs are not receiving sufficient air, pure oxygen is often given to the patient. It is also used when rendering first aid in cases of suffocation or drowning, and for renewing the atmosphere in places where the air is impure or ventilation is bad, as in mines or submarines. Oxygen, as we have seen, forms $\frac{1}{5}$ of the atmosphere by volume and forms $\frac{8}{9}$ of water by weight. It can be obtained from water by Electrolysis, a process which we will study later, but when required for commercial purposes in large quantity is usually taken from the atmosphere. Air, which is a mixture of oxygen and nitrogen, can be converted into liquid, or liquefied, by the use of great pressure at a low temperature, and can only be kept liquid under these conditions. If the pressure is decreased or the temperature raised the liquid begins to boil. The boiling point of oxygen is -182° , and that of nitrogen -194° . Nitrogen has thus a lower B.P. and boils off first, leaving liquid oxygen behind, which is then allowed to boil and the gas forced under pressure into steel cylinders. Oxygen has great chemical activity and unites with most other elements to form oxides

This union takes place as a rule more readily at high temperatures and is then known as combustion, giving light and heat.

Preparation of Oxides

EXPT.—Prepare from oxygen mixture or draw off from a cylinder of the gas sufficient oxygen to fill half a dozen gas jars, and see that these are well covered with greased glass plates. Take a small piece of charcoal, place it in a Deflagrating Spoon and heat in the Bunsen flame till it begins to glow, then remove one of the glass covers and plunge the spoon into the jar. Note that the charcoal glows much more brightly. When combustion has ceased, shewing that the oxygen has been used up, remove the spoon, pour a little lime water into the jar, replace the cover and shake. Observe that the lime water has turned milky. Charcoal consists mainly of the element Carbon, and in burning it unites with oxygen to form an oxide, Carbon Dioxide. Repeat the experiment, adding instead of lime water, litmus solution. Note any change of colour.

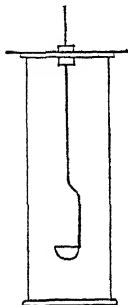


FIG. 18.

Carbon dioxide is a colourless and odourless gas which turns lime water milky and gives a red colour with purple litmus.

EXPT.—Take a little sulphur in a spoon and heat in the flame till it burns, then transfer to an oxygen jar as before. It burns more brightly with a blue flame. After combustion is over, pour a little water into the jar, cover and shake. Pour the liquid into a beaker, note its pungent choking smell, and add some litmus solution or dip into it a piece of litmus paper. Observe the change of colour.

As in the last experiment, an oxide has been formed known as Sulphur Dioxide. This is also a colourless gas but has a strong odour. Made in this way it is cloudy, as a small quantity of another oxide of sulphur, Sulphur Trioxide, is formed at the same time which gives this appearance.

EXPT.—Take a stick of phosphorus out of the bottle with a crucible tongs, cut off a piece and dry it, observing the usual precautions. Place in a spoon, warm in the Bunsen flame and transfer quickly to an oxygen jar. It burns with a brilliant white flame, giving off white clouds of Phosphorus Pentoxide. When it is burnt out add some water and shake up. Test again with litmus.

Carbon dioxide and sulphur dioxide are colourless gases. Phosphorus pentoxide is a white solid. Carbon dioxide dissolves slightly in water. Sulphur dioxide and phosphorus pentoxide dissolve readily, indeed the latter has such a strong attraction for water that it is used for drying gases. These oxides combine with water to form *acids*, a class of substances which will be described later, giving respectively, carbonic acid, sulphurous acid and phosphoric acid. Oxides which act in this way are called **Acidic Oxides** or **Anhydrides**—a word meaning ‘without water.’ Litmus is a colouring matter derived from plants. Its solution, or ‘litmus paper’ made by dipping absorbent paper in the solution and drying, is used in testing for acids. The solution is most sensitive when of a purple colour, and the papers are coloured blue and red. Acids turn litmus solution and blue litmus paper red. Carbonic acid is a weak acid and it will be observed that it does not give such a distinct red as the stronger sulphurous and phosphoric acids.

Some elements which burn in oxygen do not give acid oxides.

EXPT.—Twist a few inches of magnesium ribbon into a spiral. Remove the spoon from the cork which supports it and fix the spiral between the cork and cover. Ignite the free end in the flame and lower it quickly into a jar of oxygen. It burns brilliantly, forming magnesium oxide. Collect the white powder and place it upon a moistened piece of red litmus paper; after a little time the paper turns blue.

Magnesium oxide is evidently not an acidic oxide, as a solution of an acidic oxide in water turns litmus red. This kind of oxide, of which there are many, is called a **Basic Oxide**. When basic oxides unite with water they do not form acids, but give substances known as hydroxides.

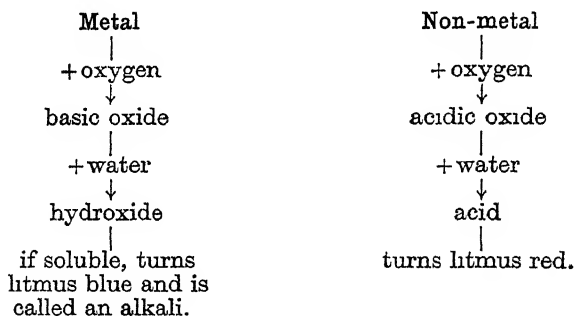
EXPT.—Take a small piece of sodium and dry it carefully. Place in a spoon and heat in the flame until it takes fire, then transfer to a jar of oxygen. When combustion ceases add a little water and test with red litmus paper. Sodium oxide evidently belongs to the same class as magnesium oxide.

NOTE. *Experiments involving the combustion of sodium and potassium are always attended by a certain amount of risk, as particles of the substance are apt to fly off and may cause severe burns. Great care must be taken and the minimum quantity used.*

The performance or omission of such experiments is left to the discretion of the teacher.

Most hydroxides are insoluble in water and consequently cannot be tested with litmus paper, but when they dissolve, the solution turns litmus paper blue. Such soluble hydroxides are called *alkalies*. A solution which turns litmus blue is said to be *alkaline*, and one which turns litmus red is said to be an *acid* solution. When sodium oxide unites with water it forms sodium hydroxide which dissolves in the water giving an alkaline solution.

EXPT.—Test with litmus paper solutions of caustic potash, hydrochloric acid, ammonia solution, sulphuric acid, acetic acid, lime water, and caustic soda. Classify these substances into alkalies and acids.



Additional Experiments

EXPT.—Heat a number of different oxides and test for oxygen. Copper oxide, manganese dioxide, lead monoxide, lead peroxide, barium oxide, ferric oxide, red lead.

EXPT.—Heat some potassium chlorate in a porcelain basin till oxygen is just beginning to come off. Remove the flame and add a few grains of manganese dioxide. Note the rush of oxygen and the heat given out.

EXPT.—To burn iron in oxygen. Plait together 2 or 3 strands of very fine iron wire and tip the end with molten sulphur. Ignite it, and when the sulphur is burning freely plunge into a jar of oxygen. Observe the coruscating effect of the burning iron. A little sand may be placed on the bottom of the jar to protect the glass.

QUESTIONS

1. By whom was oxygen discovered and how? Who named the gas oxygen and for what reason? Describe how the element is usually prepared and collected. (London Matric.)

2. Give some account of the Phlogiston theory, and tell what you know of the work of Lavoisier in establishing the accepted explanation of the gain of weight during the calcination of metals. (Scot. Univ. Entrance.)

3. Describe the method by which Priestley originally made oxygen and give details of any other methods which you think are more convenient for laboratory use. What experiments would you perform in order to demonstrate the principal properties of oxygen?

4. Describe and explain any process by which pure oxygen can be obtained from the atmosphere.

5. Give full details of an experiment for finding the weight of 1 litre of oxygen, and show how the weight may be calculated from your experimental results.

6. What are oxides? Describe carefully any experiments you have carried out or seen carried out for the purpose of making oxides. Give an account of two classes of oxides, stating their chemical properties and the substances formed when they react with water.

CHAPTER VI

ELEMENTS AND COMPOUNDS. LAWS OF DEFINITE AND MULTIPLE PROPORTIONS

Elements and Compounds. Substances may be divided into two classes, elements and compounds. In the last chapter oxygen is called an **Element**. 'Elementary' means 'simple,' and oxygen is an elementary or simple substance. We have made sulphide of iron by combining iron and sulphur, but we cannot make either iron or sulphur by the union of other substances. Mercuric oxide when heated decomposes into mercury and oxygen, but no chemist has ever succeeded in decomposing mercury or oxygen. An elementary substance or **Element** may be defined as 'a substance which we cannot decompose, or make by the combination of other substances.' The result of chemical action on an element is always an increase of weight, never a decrease. Compounds, on the other hand, can be made by the combination of elements. We have made oxides by burning carbon, sulphur, phosphorus and magnesium in oxygen. All these five are elements. Compounds can also be decomposed into two or more substances by chemical methods. About ninety elements are known, but many of these are rare and seldom met with. The elements are mainly found in combination; only a few, such as oxygen, nitrogen, silver and gold, are found naturally in the elementary state. In the atmosphere, the seas and the earth's crust, taken together, the most abundant elements are as follows :

Oxygen	-	-	49.2%	Potassium	-	2.4%
Silicon	-	-	25.7 „	Magnesium	-	1.9 „
Aluminium	-	-	7.4 „	Hydrogen	-	0.9 „
Iron	-	-	4.7 „	Titanium	-	0.6 „
Calcium	-	-	3.4 „	Chlorine	-	0.2 „
Sodium	-	-	2.6 „	Carbon	-	0.2 „

These are percentages by weight.

Law of Definite Proportions. It has already been said that constancy of composition is a property of a true chemical compound. Ferrous sulphide can be made by methods other than the direct union of iron and sulphur, but whatever method be used, it is found that in every case 56 parts of iron unite with 32 parts of sulphur by weight. When mercuric oxide is heated it decomposes into mercury and oxygen. The proportions by weight are :

433 parts of mercuric oxide give 401 of mercury and 32 of oxygen.

Mercuric oxide can be made by several different methods, but it always decomposes in the above proportions. The French chemist Proust (1799) analysed specimens of the same naturally occurring substance from different parts of the world, and also analysed a large number of compounds prepared in his own laboratory. As the result of his researches he deduced the Law of Definite Proportions, which may be stated thus : 'when elements combine, they do so in definite proportions by weight, or, the composition of a chemical compound never varies.'

Law of Multiple Proportions. Two elements may sometimes combine in more than one proportion, forming in each case a different compound. Copper forms two compounds with oxygen, and mercury unites with chlorine in two proportions. From the analysis of such compounds the Law of Multiple Proportions has been deduced : 'when two elements unite to form more than one compound, the quantities of the element which varies bear to each other a ratio of small integral numbers.'

The elements mercury and iodine unite to form two compounds, in which the proportion of iodine varies.

Making the Iodides of Mercury. Let us make two or three preliminary experiments with mercury and iodine to show some of the properties of these elements.

Expt.—Heat a little iodine in a test tube, it does not melt but changes into a purple vapour. This process is called Sublimation. The iodine sublimates without melting and condenses on the cooler part of the tube, forming a crystalline deposit called the Sublimate. These terms are only applied to solids.

Expt.—Shake up some iodine in a test tube with water, alcohol, and carbon disulphide successively and observe the colours of the solutions. Add a few drops of carbon disulphide to the water

solution and shake; the carbon disulphide collects all the iodine, shewing that it is a better solvent for iodine than water. Add water to the alcoholic solution, some of the iodine falls to the bottom; it is more soluble in alcohol than in water.

EXPT.—Heat some mercury in a test tube till it boils, changing into a colourless vapour which condenses on the colder part of the tube. This process is called Distillation, a term which is only applied to liquids.

EXPT.—To make the two compounds of mercury and iodine. Weigh out 2 parts of mercury and 2.6 parts of iodine. Transfer to a mortar and moisten the iodine with alcohol. Grind the substances together with a pestle till they unite to form a red compound; this is the compound containing the greater amount of iodine and is known as **Mercuric Iodide**.

Weigh 2 parts of mercury and 1.3 parts of iodine and treat in the same way. This gives a green compound containing the smaller proportion of iodine, which is called **Mercurous Iodide**. These are the theoretical quantities, but a small excess of iodine in the first, and of mercury in the second case, may be used.

Note that the names of these compounds as well as those of ferrous sulphide and mercuric oxide end in 'ide.' The rule is that when only two elements unite to form a compound the name of the second is modified so that it ends in 'ide.' Note also the ending 'ic' (mercuric) given to the compound containing the greater proportion of iodine, and the termination 'ous' of the compound containing the smaller proportion.

The law of multiple proportions can be illustrated quantitatively by the following experiment

EXPT.—Weigh a 100 c.c. beaker accurately and place in it about 5 grams of mercurous chloride, also accurately weighed. Add 30 c.c. of water, heat on a water bath and pour into the beaker 5-10 c.c. of hypophosphorous acid. The mercurous chloride is soon reduced to metallic mercury, which on further heating collects into globules. The metal is then washed by decantation with water, alcohol and ether in succession. To wash by the method of decantation, pour a little water into the beaker and swirl it round for a few moments, then pour off the water carefully. Repeat this two or three times, then remove the last drops of water by sucking it up with a piece of filter paper. Repeat this process with alcohol and ether and finally dry for five minutes in a drying oven or over a very small flame. Ether is very inflammable, so take care that there is no light near when it is being used. Allow the beaker to cool, and weigh. Subtract the weight of the

beaker to find the weight of mercury obtained. Next weigh out 5 grams of mercuric chloride and treat it in exactly the same way. Mercurous chloride and mercuric chloride are both compounds of mercury and chlorine, but the second contains twice as much chlorine as the first.

Calculation.

4.87 grams of mercurous chloride gave 4.13 grams of mercury;
4.87 grams contained $4.87 - 4.13 = 0.74$ gram of chlorine.

5.15 grams of mercuric chloride gave 3.80 grams of mercury,
5.15 grams contained $5.15 - 3.80 = 1.35$ grams of chlorine.

We must now calculate the weights of chlorine which will in each case combine with a fixed weight of mercury, say 100 grams.

In mercurous chloride $\frac{100 \times 0.74}{4.13} = 17.8$ grams of chlorine will combine with 100 grams of mercury.

In mercuric chloride $\frac{100 \times 1.35}{3.8} = 35.5$ grams of chlorine will combine with 100 grams of mercury; thus the quantities of the element which varies bear to each other the ratio 17.8 : 35.5, or 1 : 2.

Chlorine unites with iron in two proportions to form ferrous chloride and ferric chloride. The percentage composition is :

	Iron %.	Chlorine %
Ferrous chloride - - -	44.05	55.95
Ferric chloride - - -	34.42	65.58

Calculate the chlorine ratio, that is, the ratio of the weights of chlorine which combine with a fixed weight of iron, say 100 grams.

In ferrous chloride $\frac{55.95 \times 100}{44.05} = 127.0$ grams of chlorine combine with 100 grams of iron.

In ferric chloride $\frac{65.58 \times 100}{34.42} = 190.5$ grams of chlorine combine with 100 grams of iron. The chlorine ratio is then 127 : 190.5. Dividing each of these numbers by 127, we get the ratio 1 : $1\frac{1}{2}$, or 2 : 3. Thus the quantities of the element which varies bear to each other the ratio 2 : 3, a ratio of small integral numbers.

Examples to be Worked

1. There are two different compounds of copper with oxygen, red cuprous oxide and black cupric oxide. In this case the proportion of copper varies. The percentage composition of these oxides is :

	Copper %.	Oxygen %.
Red cuprous oxide - -	88.8	11.2
Black cupric oxide - -	79.9	20.1

Calculate the copper ratio, that is, the ratio of the weights of copper which combine with a fixed weight of oxygen, say 10 grams.

2. The compounds of mercury with iodine, in which the proportion of iodine varies, have the following percentage composition :

	Mercury %.	Iodine %.
Mercurous iodide - -	61.24	38.76
Mercuric iodide - -	44.14	55.86

Calculate the iodine ratio.

3. Tin unites with oxygen forming two oxides in which the proportion of oxygen varies. The percentage composition is :

	Tin %	Oxygen %
Tin monoxide - - -	88.12	11.88
Tin dioxide - - -	78.77	21.23

Calculate the oxygen ratio.

4. Phosphorus forms two compounds with chlorine, in which the proportion of chlorine is different. The percentage composition is :

	Phosphorus %	Chlorine %
Phosphorous chloride - -	22.58	77.42
Phosphoric chloride - -	14.89	85.11

Calculate the chlorine ratio.

5. The five oxides of nitrogen are the most striking example of the law of multiple proportion. The percentage compositions are :

	Nitrogen %	Oxygen %.
Nitrous oxide - - -	63.7	36.3
Nitric oxide - - -	46.7	53.3
Nitrogen trioxide - -	36.9	63.1
Nitrogen peroxide - -	30.5	69.5
Nitrogen pentoxide - -	25.9	74.1

Calculate the proportions of oxygen in these five compounds.

Additional Experiments

EXPT.—To illustrate the law of definite proportions. Prepare copper oxide by heating several different substances, such as copper nitrate, copper carbonate, and copper hydroxide. Make a boat of copper foil and place in it a definite weight of each specimen of copper oxide. Heat in a combustion tube in a current of coal gas. When reduction is complete remove heat and allow to cool in the gas. Weigh the resulting copper and calculate the percentage, which should be the same in each case.

EXPT.—To illustrate the law of multiple proportions. Reduce weighed quantities of black cupric oxide and red cuprous oxide as in the last experiment. Weigh the reduced copper and calculate the percentage composition and the copper ratio.

QUESTIONS

1. Explain the meaning of the term 'element,' and mention the six chemical elements which occur most abundantly in nature.

2. Classify the following substances into elements and compounds: baking soda, black lead, caustic soda, diamond, flowers of sulphur, gypsum, plastic sulphur, quicklime, quicksilver, white lead. (Scot. Univ. Entrance.)

3. Describe a laboratory experiment in illustration of the law of chemical combination in multiple proportions. (Oxford and Camb. School Cert.)

4. State the Law of Definite Proportions and the Law of Multiple Proportions. Illustrate the truth of these laws by reference to any compounds with which you are familiar. 3.6 grams of the puce-coloured oxide of lead were heated gently in a stream of hydrogen. The substance became yellowish in colour and on cooling was found to weigh 3.359 grams. The residue was then heated more strongly in the stream of hydrogen, and metallic beads were formed which weighed 3.118 grams. Interpret these results as fully as you can. (Scot. Leaving Cert.)

5. State the Law of Multiple Proportions, and give illustrative examples, (a) among nitrogen compounds, (b) among carbon compounds. (Scot. Univ. Entrance.)

CHAPTER VII

THE GAS LAWS

The Gas Laws. In discussing such a subject as the atmosphere, we have found the necessity of measuring gases accurately by volume, and this is in general a much easier method than weighing them. Now the volume of a gas is altered by changes of pressure and temperature, and to be able to calculate the effect of such changes we must familiarise ourselves with the gas laws.

Boyle's Law. The volume of a gas is the space which it occupies. If a gas be compressed it is squeezed into a smaller volume and its particles come closer together. The opposite is also true, that if the pressure of a gas be reduced by enlarging the space in which it is contained, it will expand and fill the new space, its volume being thus increased. This expansion is due to the activity of the gas particles whose constant motion carries them to all parts of the enclosing vessel.

There is a fixed relationship between the pressure and volume of a definite weight of any gas. This is expressed in the law discovered by Robert Boyle in the year 1661, known as Boyle's Law. 'The volume of a gas varies inversely as the pressure, provided it is kept at a constant temperature.' This proviso is necessary as the volume is affected by temperature as well as pressure. Let us suppose that we have a cylinder full of air with a tight-fitting piston, and that with one atmosphere of pressure the piston is just at the top of the cylinder. If we increase the pressure on the piston to two atmospheres, the volume of the gas will be reduced to one-half. An increase of pressure to three atmospheres gives a reduction of volume to one-third, and an increase to four a reduction to one-fourth. The volume thus varies inversely as the pressure.

Now multiply the pressure by the volume in each case :

$1 \times 1 = 1$, $2 \times \frac{1}{2} = 1$, $3 \times \frac{1}{3} = 1$, $4 \times \frac{1}{4} = 1$. Or, if we suppose that the volume of the gas is in the first case 600 c.c., in the second case it will be 300 c.c., in the third 200 c.c., and in the last case

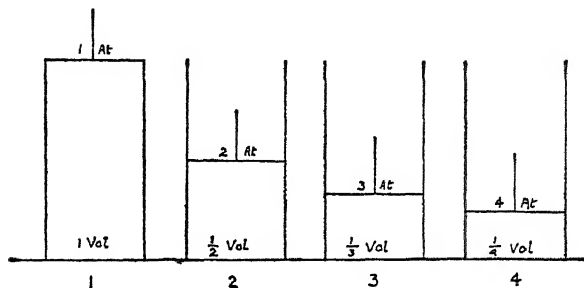


FIG. 19.

it will be 150 c.c. Multiply these volumes by the corresponding pressures :

$$600 \times 1 = 600, \quad 300 \times 2 = 600, \quad 200 \times 3 = 600, \quad 150 \times 4 = 600.$$

From this we learn that the product of the pressure and the volume is constant. If P represents the pressure and V the volume, we derive the expression, $PV = \text{constant}$. Compare cases 1 and 2 above. In case 1 represent the pressure by P and the volume by V , in case 2 by P' and V' . The pressures and volumes are different but the products are the same, therefore $PV = P'V'$. Given three of these quantities we can find the fourth.

Consider the following problem : 1000 c.c. of gas at a pressure of 4 atmospheres has its pressure changed to 16 atm (the temperature being constant), what is the new volume ?

1000 c.c. of gas at 4 atm.

x c.c. „ at 16 atm.

Increase of pressure reduces the volume, so multiply by the smaller pressure and divide by the larger, thus :

$$x \text{ c.c.} = 1000 \text{ c.c.} \times \frac{4}{16} = 250 \text{ c.c.}$$

Again, 1000 c.c. of gas at 8 atm. pressure has its pressure changed to 1 atm at constant temperature, what is the new volume ?

1000 c.c. of gas at 8 atm.

x c.c. „ at 1 atm.

Decrease of pressure increases the volume, so multiply by the greater pressure and divide by the smaller :

$$x \text{ c.c.} = 1000 \text{ c.c.} \times \frac{8}{1} = 8000 \text{ c.c.}$$

In these and all similar problems, note that the original volume is multiplied by the original pressure and divided by the final pressure to obtain the final volume. Representing the original volume and pressure by V and P , and the final volume and pressure by V' and P' , we derive the expression :

$$1. \quad V' = V \times \frac{P}{P'}.$$

The average pressure of the atmosphere is equal to the pressure of a column of mercury 30 inches or 760 millimetres high, and in comparing volumes of gases they are reduced by calculation to the volumes which they would occupy at 0° Centigrade and 760 mm. These conditions are known as **Normal Temperature and Pressure**, or **N.T.P.**

Charles' Law. The volume of a gas is also affected by change of temperature, it is increased by heating and diminished by cooling. The law showing the relationship between volume and temperature was announced by Gay Lussac in 1802, but is generally called **Charles' Law** after J. A. Charles of Paris, who had already discovered the facts in 1787. This name also prevents confusion with another chemical law known as Gay-Lussac's Law. The law states that 'The volume of a gas, at constant pressure, increases by $\frac{1}{273}$ of its volume at 0° C. for every degree rise of temperature.' It also diminishes in the same way with fall of temperature. Thus, a quantity of gas which measures 273 c.c. at 0° C. becomes at 100° , 373 c.c., and at -100° , 173 c.c. The temperature -273° C., that is, 273° below the freezing point of water, is supposed to be the lowest that it is possible to attain, and is called the **Absolute Zero**, and a scale of temperature founded upon the absolute zero is known as the **Absolute Scale**. According to the terms of this law, if a gas is cooled to -273° C. its volume is zero, that is, it occupies no space, which of course is impossible, if the law of the indestructibility of matter is true. When we talk of the volume of a gas we really mean the space between its particles, and it is that space which theoretically disappears when the particles become squeezed together. But every gas when cooled be-

comes liquefied before the absolute temperature is reached, and after that does not obey the gas laws.

On the absolute scale 0°C. becomes 273° , 100°C. becomes 373° , and -20°C. , that is, 20 degrees below the freezing point, becomes $-20 + 273 = 253^{\circ}$. Any centigrade temperature can be converted into absolute temperature by adding to it 273.

We can state Charles' Law in another form, 'The volume of a gas varies as its absolute temperature.' To illustrate this by a problem: 20 c.c. of gas at 19°C. is cooled to 0°C. , the pressure remaining unchanged at 760 mm. What is the new volume? We have here again four quantities, and if we know three we can calculate the fourth, thus:

20 c.c. of gas at 19°C.

x c.c. ,, at 0°C.

First convert centigrade into absolute temperature.

20 c.c. of gas at 292°abs.

x c.c. ,, at 273°abs.

In this case the temperature is lowered, therefore the volume must be less, so we multiply by the smaller absolute temperature and divide by the greater.

$$x = 20 \times \frac{273}{292} = 18.7 \text{ c.c.}$$

Vary the problem again. Under the same conditions what would the volume of the gas be at 100°C. ?

20 c.c. of gas at 19°C.

x c.c. ,, at 100°C.

In this case the temperature is raised, consequently the volume is increased, and we multiply by the greater absolute temperature and divide by the smaller.

$$x = 20 \times \frac{373}{292} = 25.5 \text{ c.c.}$$

In these and all similar problems observe that the original volume is multiplied by the final absolute temperature, and divided by the original absolute temperature to obtain the final volume. Representing the original absolute temperature by T and the final absolute temperature by T' , we derive the expression:

$$2. \quad V' = V \times \frac{T'}{T}.$$

Let us now take a problem involving a change of both pressure and temperature. A quantity of gas occupies a volume of 40 c.c. at 18°C . and 770 mm., calculate its volume at 0°C . and 760 mm. (N.T.P.). Convert centigrade into absolute.

40 c.c. of gas at 291°abs. and 770 mm.

x c.c. ,, 273°abs. and 760 mm.

The temperature is lowered, decreasing the volume, so multiply by the smaller and divide by the larger absolute temperature. The pressure is reduced, increasing the volume, so multiply by the greater and divide by the smaller pressure :

$$x = 40 \times \frac{273}{291} \times \frac{770}{760} = 38 \text{ c.c.}$$

In expression 1. $V' = V \times \frac{P}{P'}$, note that the original pressure is always the numerator. In expression 2. $V' = V \times \frac{T'}{T}$, note that the original absolute temperature is always the denominator.

Combining expressions 1. and 2., we get the general expression 3.

$$3. V' = V \times \frac{P}{P'} \times \frac{T'}{T}.$$

Another form of this is obtained by multiplying both sides of the equation by $\frac{P'}{T'}$.

$$4. \frac{V'P'}{T'} = \frac{VP}{T} \quad \text{or} \quad \frac{VP}{T} = \frac{V'P'}{T'}.$$

Expressions 3. and 4. can be used in the solution of any problem involving Boyle's and Charles' laws. As an example, take a case where the volume and pressure are given, the temperature being the unknown quantity. Let the volume of gas be 50 c.c. at 21°C . and 700 mm. Change both pressure and temperature. Suppose the volume is now 100 c.c. and the pressure 400 mm., calculate the final temperature.

50 c.c. of gas at 21°C . and 700 mm.

100 c.c. ,, at $x^{\circ}\text{C}$. and 400 mm.

Convert to absolute temperatures :

50 c.c. of gas at 294° abs. and 700 mm.

100 c.c. ,, at x° abs. and 400 mm.

Take expression 4. and substitute the values of volume, pressure and temperature given :

$$\frac{VP}{T} = \frac{V'P'}{T'} : \frac{50 \times 700}{294} = \frac{100 \times 400}{T'} ;$$

$$\therefore T' \times 50 \times 700 = 294 \times 100 \times 400 ;$$

$$\therefore T' = \frac{294 \times 100 \times 400}{50 \times 700} = 336^{\circ} \text{ abs. or } 63^{\circ} \text{ C.}$$

Note particularly that the calculated temperature in such a problem is on the absolute scale, and is converted into centigrade temperature by subtracting 273.

The validity of Boyle's Law and Charles' Law can be tested by the following experiments.

EXPT.—Procure a small graduated glass burette, and fix it to a vertical scale. Connect it by a thick rubber tubing with a glass cistern containing mercury held in a clamp beside the scale. Open the stop-cock of the burette and adjust the mercury cistern so that the burette is nearly filled with air. Clamp the cistern in this position and note the exact quantity of air in the burette, it is then at atmospheric pressure. Close the stopcock, raise the mercury cistern about 6 inches, clamp it and measure carefully the vertical distance between the mercury levels. If the burette contained originally 20 c.c. of air, and the mercury level in the cistern is 6 inches above that in the burette, then the pressure upon the air is the atmospheric pressure of 30 inches plus 6 inches of mercury, altogether 36 inches, and

$$20 \text{ c.c.} \times \frac{30}{36} = 16 \cdot 6 \text{ c.c.}$$

The volume should thus be reduced to 16.6 c.c. Experiment with various heights of the cistern, and compare the actual with the theoretical volume of the air.

D

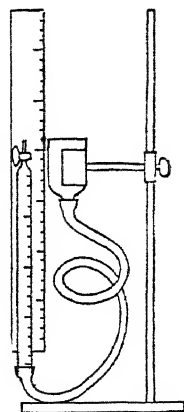


FIG 20

S S C

EXPT —Take a dry litre flask and connect it by means of a glass tube of rather small bore with a beaker of water, the tube just

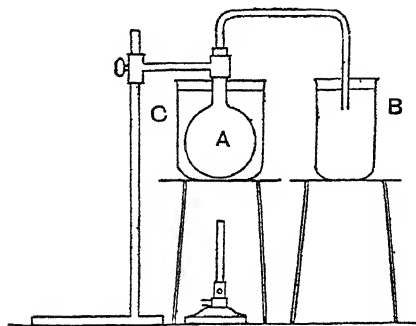


FIG 21.

dipping below the surface as shewn in the diagram. Clamp the flask in position and surround it with a large beaker or can of boiling water, immersing it as completely as possible. Continue heating until the air ceases to bubble through the water in *B*. The air is then at a temperature of 100°C . Remove the burner and the vessel *C* and allow the apparatus to cool. As the water runs back from *B* to *A*, see that the end of

the tube is kept below the surface. When the apparatus has cooled to room temperature the air which filled the flask at 100°C . occupies the space, volume of flask minus volume of water. Remove the stopper from *A*, disconnect it and measure the water in a graduated cylinder. Also measure the capacity of the flask with the stopper in place. Note the temperature of the room and find by calculation whether the result is in accordance with Charles' Law.

Example.

Volume of flask and volume of air at 100°C .	-	1020 c.c.
Volume of water run back	-	225 c.c.
Volume of air at 17°C .	-	795 c.c.

Theoretically by Charles' Law,

$$1020 \text{ c.c. at } 100^{\circ}\text{C. becomes at } 17^{\circ}\text{C. } 1020 \times \frac{290}{373} = 793 \text{ c.c.}$$

Dalton's Law of Partial Pressures. John Dalton (1802) found that in a mixture of gases, 'each gas exerts the same pressure as if it alone filled the entire space, and the total pressure is equal to the sum of the partial pressures of each component gas.' This is known as Dalton's Law of Partial Pressures. Thus if a vessel be filled with dry air at a pressure of 1 atmosphere, the pressure of the oxygen is $\frac{1}{5}$ of an atmosphere, and that of the nitrogen is $\frac{4}{5}$ of an atmosphere. If a globe contains a dry mixture consisting of $\frac{1}{3}$ oxygen and $\frac{2}{3}$ nitrogen by volume at a pressure of 900 mm., and the oxygen

be removed by some means, the remaining nitrogen will fill the globe at a pressure of 600 mm.

Additional Experiments

EXPT.—The tube known as a 'Boyle's Law tube' may also be used for measuring the effect of pressure upon volume. It consists of a piece of glass tubing, which must be of uniform bore. The tube is bent into the form of the letter J, the short limb being sealed up, and the long limb widened slightly at the upper end to form a funnel. A little mercury is introduced and the levels adjusted until they are the same; an air column is thus enclosed at atmospheric pressure in the short limb. The height of this column is measured, and successive quantities of mercury are poured into the long limb. After each addition the height of the air column and the difference between the heights of the two mercury columns are measured. The pressure upon the air is in each case this difference plus the height of the barometer at the time of measuring. Shew from these measurements that PV is constant.

EXPT.—Take a dry half-litre flask and fit it with a one-hole rubber stopper. Push into the stopper a piece of glass tubing to which is attached a couple of inches of rubber tubing carrying a spring clip. Immerse the flask up to the stopper in a beaker of boiling water, with the clip open, until the contained air is at the temperature of 100°C . Close the clip, remove the flask and place it in a pail containing ice and water, immersing it completely; open the clip under water. Then remove the flask, pour the water which has run in into a measuring cylinder and note its volume. Find the volume of the flask. The difference between these volumes is the volume of the air at 0°C . This volume increases at 100°C . to the volume of the flask. Calculate whether the increase per rise of 1°C . agrees with Charles' Law.

QUESTIONS

1. State the Laws of Boyle and Charles. What volume of dry carbon dioxide measured at 17°C . and 785 mm. pressure would be liberated from 250 grams of calcium carbonate by the action of an acid ?
(Scot. Univ. Entrance)
2. State the laws governing the behaviour of a gas, (a) when the temperature changes, (b) when the pressure changes. 10 litres of sulphur dioxide are measured at 10°C . and 800 mm. pressure, what volume will the gas occupy at N.T.P. ?

3. Sketch the apparatus you would use to determine what volume of oxygen, at N.T.P., is given off when 2 grams of potassium chlorate are heated. State exactly what you would measure, and how you would calculate the result.

(Oxford and Camb. School Cert.)

4. 1 gram of zinc, containing only oxide of zinc as an impurity, yielded on treatment with dilute sulphuric acid 130 c.c. of dry hydrogen gas measured at 15° C. and 755 mm., calculate the percentage of zinc present in the impure specimen. (zinc = 65.4)

(London Matric.)

5. State carefully and accurately the following laws: (a) Boyle's Law, (b) Dalton's Law of Partial Pressures. Two flasks contain respectively 1000 c.c. of air at 750 mm. pressure, and 500 c.c. of coal gas at 600 mm. pressure. The flasks are then connected by a tube of negligible volume. Find the pressure of the mixed gases, assuming the temperature remains constant. If the temperature be 15° C., and the gaseous mixture be then heated to 30° C., calculate the resultant pressure. (Scot. Univ. Entrance.)

CHAPTER VIII

EQUIVALENTS

If we look up our dictionaries, we find that the word 'equivalent' means 'equal in value.' Twelve pence are equivalent to one shilling, one foot is the equivalent of twelve inches. In chemistry, 'equivalent' means 'equal in combining value.' From the laws of definite and multiple proportions we have learned that each element enters into combination in a definite fixed weight, or small multiple of that weight. In order to find out and compare these weights we require a standard. Hydrogen is the lightest of all the elements, so we may meantime take one gram of hydrogen as our standard weight. The weight in grams of each element which will combine with or replace one gram of hydrogen is then equivalent to one gram of hydrogen in combining value. This is called the Equivalent or Equivalent Weight of the element, or the Gram Equivalent. Hydrogen is a suitable standard as the equivalents of all other elements are greater than that of hydrogen.

Many of the metals dissolve readily in dilute hydrochloric acid or dilute sulphuric acid, setting free hydrogen gas (all acids, as we shall see later, contain hydrogen). The metal enters into combination, taking the place of the hydrogen set free, and that weight of metal which replaces one gram of hydrogen is thus the gram equivalent of the metal. We will now try to measure the equivalents of some of the metals by this method. Let us take first the metal magnesium.

EXPT.—Weigh out about 0.04 gram of magnesium ribbon. Into a 50 c.c. burette pour 5 c.c. of concentrated hydrochloric acid, and pour water gently down the side of the burette (so as not to disturb the acid) until completely full. Drop in the piece of magnesium. Close the burette with the forefinger, invert it, quickly immerse the closed end in water in a basin, and remove the finger. As the heavier acid sinks, it comes in contact with the metal, and

hydrogen is evolved. When the magnesium is dissolved, close the burette again with the finger and transfer it to a measuring cylinder full of water. Remove the finger under water, and adjust until the water in the burette and cylinder is at the same level, when the gas is at atmospheric pressure. Read off the volume. Find the room temperature and barometric pressure, and correct the volume to N.T.P. One litre of hydrogen at N.T.P. weighs 0.09 gram.

Calculation.

Weight of magnesium	= 0.035 gram.
Volume of hydrogen	= 35.2 c.c.
Barometric pressure	= 750 mm.
Temperature	= 18° C.

Correcting volume to N.T.P., $35.2 \times \frac{750}{760} \times \frac{273}{291} = 32.5$ c.c.

1000 c.c. of hydrogen weigh 0.09 gram ;

$$\therefore 32.5 \text{ c.c. weigh } \frac{0.09 \times 32.5}{1000} = 0.00292 \text{ gram.}$$

Therefore 0.035 gram of magnesium has replaced 0.00292 gram of hydrogen. The weight of magnesium required to set free one gram of hydrogen is then $\frac{0.035}{0.00292} = 12$ grams, and the equivalent of magnesium is 12.

When a gas is measured over water, some water vapour mixes with it and increases its volume. If the utmost accuracy is required, it is necessary to make a correction for this. The pressure of the gas is the combined pressure of the hydrogen and water vapour. The pressure of water at room temperature is found from a table compiled for the purpose, and subtracted from the barometric pressure. This gives the pressure of dry hydrogen, which is used in correcting the volume to N.T.P. In the last experiment take the vapour pressure of water as 15 mm. The expression for correction of the gas volume to N.T.P. then becomes $35.2 \times \frac{750-15}{760} \times \frac{273}{291} = 31.9$, as compared with the uncorrected volume 32.5, a difference of 2%. This correction is absolutely necessary when large volumes of gas are measured over water. When dry gas is measured over mercury it is not required.

EXPT.—To find the equivalent of zinc, iron or aluminium. Arrange the apparatus as shewn. *A* is a 500 c.c. measuring cylinder. *B* is a bottle holding 2 litres, and *C* is a small flask. *A*

leading tube extends from the bottom of the bottle *B* to that of the cylinder *A*. This is broken by a piece of rubber tubing about 6 inches long, to permit of the cylinder being raised. On it is fixed a spring clip. Another piece of tube, ending just below the bottle stopper, connects it with the flask. See that all the connections are airtight. Weigh out the required quantity of metal in a small glass tube. To give about 300 c.c. of hydrogen, 0.87 gram of zinc, 0.75 gram of iron, or 0.24 gram of aluminium should be used. Pour some dilute hydrochloric acid (for aluminium equal quantities of concentrated acid and water are required) into the generating flask, and by means of a thread lower the tube into the acid, taking care that its mouth is above the acid level. Run water into the bottle *B* until nearly full, and insert the stopper with its tubes to fit tightly. Attach the flask to the bottle and open the clips to equalise the pressure. Then place the empty cylinder *A* in position and shake the flask until the acid comes in contact with the metal. The hydrogen evolved displaces the water in the bottle *B* and forces it over into the cylinder. When solution is complete and the apparatus is cool, adjust the cylinder and bottle till the water in each is at the same level, then close the clip and note the volume of the water. This is equal to the volume of the gas which has displaced it. Correct the volume to N.T.P. and calculate the equivalent of the metal as in the last experiment.

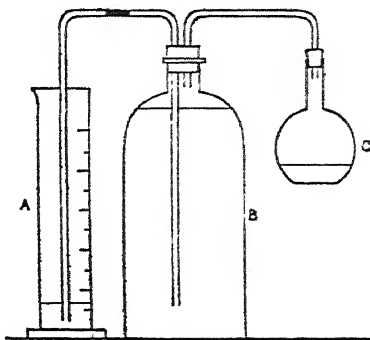


FIG 22

Just as hydrogen is displaced from acids by metals, so also some metals are displaced by others from solutions of their salts. For example, zinc and iron displace copper.

EXPT.—Test this by dipping a knife blade into copper sulphate solution. The knife blade becomes coated with copper.

Now copper does not dissolve in dilute hydrochloric or dilute sulphuric acid, so that we cannot use the method of displacement of hydrogen to estimate its equivalent. Suppose, however, that we have found by this method that the equivalent of zinc is 32.5, then the weight of copper which 32.5 grams of zinc replaces in a solution of copper sulphate is equal in combining power to 32.5 grams of zinc and consequently to 1 gram of

hydrogen, it is in fact the equivalent weight of copper. That is, if A is the equivalent weight of an element with respect to hydrogen, and B is the equivalent weight of another element with respect to A , then B is also the equivalent with respect to hydrogen. We may thus use the method of displacement of copper from copper sulphate to find the equivalent of the metal.

EXPT.—To find the equivalent of copper. Weigh out one gram of well-cleaned zinc foil. Cut into small pieces and drop it into a porcelain basin containing copper sulphate solution. A brown deposit of copper is produced, but the action may take some hours to complete. Stir occasionally with a glass rod, and if the copper sulphate solution loses its blue colour add some more. When the zinc is completely dissolved pour off the liquid, taking care that no copper goes with it. Then wash by decantation, as already explained, with hot water. Filter the copper on to a previously dried and weighed filter paper. Wash again with hot water. Test the filtrate by catching a little in a test tube and adding a little ammonia solution. If it still contains copper sulphate, the liquid will turn faintly blue. Continue washing until the test gives no blue tinge. Then remove the paper from the funnel and dry it at a low heat in an oven or spread it on a sheet of wire gauze and dry very gently over a Bunsen. Allow the paper and copper to cool and weigh. An alternative method of treatment is to wash the copper by decantation in the basin (which must have been previously weighed) with hot water, alcohol and ether, dry very gently and weigh.

Calculation.

Weight of zinc taken	= 0.97 gram.
Weight of filter paper	= 0.86 gram.
Weight of filter + copper	= 1.81 grams.
∴ Weight of copper	= 0.95 gram.

The equivalent weight of zinc = 32.5 grams,

0.97 gram of zinc displaces 0.95 gram of copper ;

∴ 32.5 grams of zinc displace $\frac{32.5 \times 0.95}{0.97}$ of copper = 31.8 grams ;

∴ the equivalent of copper is 31.8.

Almost all the elements unite with oxygen giving oxides. Now we can make a definite weight of an element combine with oxygen and from the increase of weight find out the quantity of oxygen with which it combines. If we know the

equivalent of oxygen we can calculate from this the equivalent of the element. It can be shewn that 8 grams of oxygen unite with 1 gram of hydrogen, so the equivalent of oxygen is 8. This gives us a third method of estimating the equivalent of an element to which the two previous methods are not applicable.

EXPT.—To measure the equivalent of sulphur. The sulphur is burned in a current of oxygen, the sulphur dioxide which is

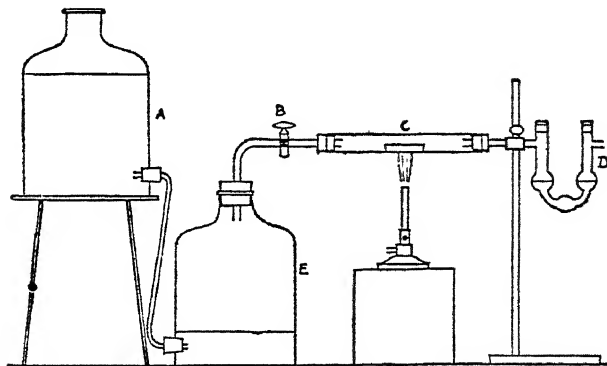


FIG 23

formed is absorbed in caustic potash and its weight found. Subtracting from this the weight of the original sulphur, we get the weight of oxygen with which it has united.

The apparatus is fixed up as in the drawing. The vessel *E* contains oxygen kept under pressure by the water in vessel *A*. *C* is a porcelain boat in a hard glass tube. One end of this tube is connected with *E* by a piece of glass tubing provided with a stop-cock *B*. The other end is connected with potash bulbs at *D*. Weigh the porcelain boat, add 1-2 grams of sulphur and weigh again. Place the boat in the combustion tube. See that the potash bulbs are filled with fresh caustic potash solution and that they are wiped perfectly clean and dry. Weigh them carefully and attach them to the combustion tube. Open the tap *B* and adjust it so that a slow current of oxygen bubbles through the potash. Heat the boat very gently until the sulphur burns, but take care that it does not boil. When it is completely burnt, continue the current for a minute or two longer, close the tap and weigh the bulbs. If thought necessary, a calcium chloride tube may be inserted between *E* and *C* to dry the oxygen.

Calculation

1st weight of potash bulbs	= 148.364 grams.
2nd weight of potash bulbs	= 151.264 grams.
Weight of sulphur dioxide	= 2.90 grams.
Weight of sulphur burned	= 1.465 grams.
Weight of oxygen combined	= 1.435 grams.

\therefore 1.435 grams of oxygen combine with 1.465 grams of sulphur, and 8 grams of oxygen combine with $\frac{8 \times 1.465}{1.435} = 8.1$ grams of sulphur. But the equivalent weight of oxygen is 8 ;

\therefore the equivalent weight of sulphur is 8.1.

A fourth method of measuring the equivalent of an element is the converse of the last method. Instead of taking an element and adding oxygen to it, we may take an oxide and remove oxygen from it. Copper oxide is very suitable for this purpose.

EXPT.—Fit up the apparatus as shewn. *A* is a hydrogen generator. *B* is a calcium chloride tube to dry the hydrogen.

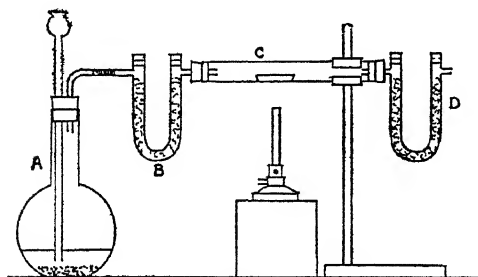


FIG. 24.

C is a hard glass tube, and *D* is another calcium chloride tube to collect the water formed (this tube is not really necessary, but is attached as it is required in a later experiment using a similar apparatus). Weigh the combustion tube *C*, place in it about 8 grams of copper oxide and weigh again. Pass a

stream of hydrogen (coal gas may be used) through the apparatus for a few minutes to expel air.

It is not safe to heat or light a mixture of hydrogen and air (or coal gas and air), as there may be a violent explosion.

In such cases, collect a little of the issuing mixture of hydrogen and air occasionally in a test tube over water and test with a lighted taper. When the gas burns quietly without any 'pop,' heat may be safely applied. When the air is

expelled heat the oxide with the Bunsen flame. Keep all the tube warm to prevent any water condensing in it. When the substance has turned completely red, cease heating, but continue to pass hydrogen till the copper is cool. Weigh the combustion tube when it is quite cold. The loss of weight is the weight of oxygen contained in the copper oxide.

Calculation

$$\begin{aligned}\text{Weight of copper oxide} &= 8.6 \text{ grams.} \\ \text{Weight of copper} &= 6.87 \text{ grams.} \\ \therefore \text{Weight of oxygen in oxide} &= 1.73 \text{ grams.}\end{aligned}$$

1.73 grams of oxygen unite with 6.87 grams of copper.

\therefore 8.0 grams of oxygen unite with 31.8 grams of copper.

but 8 is the equivalent of oxygen.

31.8 is the equivalent of copper.

There are other methods of measuring equivalents which we shall consider later.

Additional Experiments

EXPT.—To find the equivalent of silver. Weigh a porcelain basin, and place in it about 0.2 gram of magnesium cleaned from oxide with a piece of emery paper. Add a strong solution of silver nitrate. When all the magnesium has disappeared, allow the silver to settle and wash it by decantation with water and alcohol. Dry at a gentle heat. Weigh basin and silver and calculate the equivalent, taking the equivalent of magnesium as 12.

EXPT.—To find the equivalent of lead by displacement with zinc. Take a 200 c.c. beaker. Add about 100 c.c. of water and 3 grams of lead acetate. Warm, and add acetic acid drop by drop until clear. Put into the solution 0.3–0.4 gram of zinc foil in small pieces. Allow to stand for a week. Decant most of the clear liquid and pour the remainder, liquid and solid, on to a previously dried filter paper. Collect a little of the filtrate in a test tube and add a drop or two of dilute sulphuric acid which gives a milkiness if lead acetate is present, and a drop or two of ammonia solution which gives a milkiness with zinc acetate. Wash thoroughly with hot water, applying these tests at intervals till they give no result. Dry paper and lead at a low temperature in an air oven, cool and weigh. Calculate the equivalent as before.

EXPT.—To find the equivalent of tin. Weigh a clean dry test tube. Place in it about 1 gram of tin and re-weigh. Add nitric

acid very gradually until the tin is completely converted into white oxide, holding the tube in a sloping position to prevent loss by spirting. Then clamp it on a retort stand and heat carefully with the Bunsen flame, shaking occasionally, until quite dry. When cool weigh the tube. The increase of weight is the weight of oxygen which has combined with the tin. Calculate the equivalent in the usual way.

EXPT.—To find the equivalent of oxygen. Fit up the apparatus used in the fourth method of finding the equivalent, depriving copper oxide of oxygen. Use the same quantity of copper oxide and attach the *D* calcium chloride tube. The hydrogen removes oxygen from the oxide and combines with it to form water which is absorbed in the calcium chloride tube. The decrease in weight of the oxide gives the weight of oxygen and the increase in weight of the tube *D* gives the weight of water formed. From weight of water subtract weight of oxygen to get weight of hydrogen combined with it. From these data calculate the equivalent of oxygen.

EXPT.—To reduce oxides of lead by heating them in coal gas and to compare the equivalents of lead calculated from the results. Take litharge and lead peroxide. Heat two or three grams of each in a boat in a combustion tube, passing coal gas through the tube. Weigh the resulting lead in each case and subtract from the weight of oxide, obtaining the weight of combined oxygen. Calculate the equivalents of lead, taking the equivalent of oxygen as 8. This experiment may also be used as an illustration of the law of multiple proportions.

QUESTIONS

1. State clearly what is meant by the equivalent weight of an element, and write short notes on four different methods of determining equivalents. Describe in detail the method you would adopt to find the equivalent of copper. (Scot. Leaving Cert.)

2. Define the combining (or equivalent) weight of an element. Describe accurately and in detail how you would find the combining weight of (a) zinc, (b) copper. The combining weight of zinc is 32.5, and its atomic weight is 65. Explain this. (Scot. Univ. Entrance.)

3. When aluminium is dissolved in caustic soda and the liberated hydrogen burnt, the weight of water thus produced is equal to the weight of metal dissolved. From this relation calculate the equivalent weight of aluminium. (Oxford and Camb. School Cert.)

4. 0.315 gram of magnesium dissolved in hydrochloric acid gave 306 c.c. of hydrogen at 12° C. and 760 mm. pressure. Calculate the equivalent of magnesium.

5. Some iron filings were placed in copper sulphate solution, and after complete solution of the iron had taken place, the precipitated copper was filtered off, washed, dried and weighed. The weight was found to be 5.678 grams. What was the weight of the iron filings? Suppose the equivalent of iron is 28, what is the equivalent of copper? ($\text{Fe} = 56$; $\text{Cu} = 63.6$.)

CHAPTER IX

THE ATOMIC THEORY. GAY-LUSSAC'S LAW. AVOGADRO'S HYPOTHESIS

THE law of the conservation of mass, the laws of definite and multiple proportions, the theory of equivalents, all go to shew that the chemical elements, when they combine, do so in definite weights. It seems as if an elementary substance were made up of small packets, all of the same weight, the packet of each element differing in weight from those of all others. When combination takes place between two elements *A* and *B*, one or more packets of *A* unite with one or more packets of *B*. Further, these packets are never broken up, they unite together and separate as whole packets. If this were the case, we should have a complete explanation of the laws mentioned above.

The Atomic Theory. This explanation was first proposed by John Dalton (1802), a schoolmaster of Manchester. He did not use the word 'packets,' but called them 'atoms,' a word derived from the Greek, meaning 'something which cannot be cut.' Dalton's explanation is known as the **Atomic Theory**, and may be summarised as follows :

1. The chemical elements are made up of very small particles called atoms, which cannot be subdivided by chemical processes.
2. The atoms of the same element are similar in every way, and they are all of the same weight. Atoms of different elements differ in weight and other properties.
3. Compounds are formed by the union of atoms of different elements in proportions which can be represented by whole numbers, e.g. 1:1, 1:2, 2:3, 1:3, etc.

The word 'atom' signifies 'that which cannot be cut,' and the atom was until recent years supposed to be indivisible, but

it is now established that it is made up of still smaller particles known as 'protons' and 'electrons,' which are respectively, unit charges of positive and negative electricity. All matter is thus finally of electrical origin. The atom, however, passes through *chemical* reactions unchanged, and for the purposes of the chemist it is regarded as indivisible. An atom is sometimes defined as 'the smallest particle of matter which can take part in a chemical change or reaction.'

Molecules. Atoms have such a strong attraction for one another that they cannot exist alone, but unite with other atoms. The groups thus formed are called Molecules. A molecule may be defined as 'the smallest quantity of matter which can have an independent existence, and in which the original properties of the matter are retained.' The molecules of all kinds of matter, whether solid, liquid or gaseous, are in a state of constant motion. The motion is greatest in a gas, less in a liquid and least in a solid. A molecule moves about as a whole, and its constituent atoms do not part company during this motion.

The molecule of an element contains only one kind of atom, hence an element cannot be split up into any other substances. The molecule of a compound is composed of atoms of different kinds, so that a compound can be broken up into two or more different substances. In a physical change the molecules are not broken up, so that there is no change in the composition of the substance. In a chemical change the molecules are decomposed, with formation of new and different molecules. We may consider that in a chemical reaction the molecules are broken up into atoms, which, as they cannot exist alone, instantaneously group themselves differently to form new molecules and consequently a new substance or substances.

It is said that if a drop of water were magnified to the size of the earth, the molecules would appear about the size of marbles, so that they are far beyond the range of the most powerful microscope.

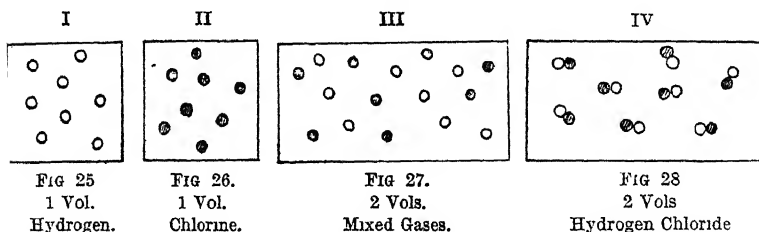
Gay-Lussac's Law. The elements then combine in simple proportions which can be represented by small whole numbers. The elementary gases, oxygen, hydrogen, nitrogen and others, combine in definite proportions by weight, but is there any simple relationship between the volumes of gases combining together? Experiment shews that there is, that gases combine in simple proportions by volume. The following are examples.

2 vols. hydrogen unite with 1 vol. oxygen, giving 2 vols. steam.
 3 vols. hydrogen unite with 1 vol. nitrogen, giving 2 vols. ammonia. 1 vol. hydrogen unites with 1 vol. chlorine, giving 2 vols. of hydrogen chloride or hydrochloric acid. All other gases when they combine do so in simple proportions by volume.

Gay-Lussac (1808), after a careful investigation of the chemical reactions between gases, proposed the following law. 'When gases react together, they do so in volumes which bear a simple ratio to one another, and to the volume of the gaseous product of the reaction.' As combination presumably takes place between the gas particles, Gay-Lussac conceived the idea that there must be some simple relationship between the number of particles in equal volumes of different gases.

Lord Kelvin, the famous mathematician and physicist, once said, "I never satisfy myself that I understand a problem in physics until I can make a mechanical model of it." Similarly, we can understand the mechanism of a chemical reaction better if we can draw a picture of it. Take the combination of the two gases hydrogen and chlorine. By experiment it is found that one volume of hydrogen unites with one volume of chlorine to form two volumes of hydrogen chloride.

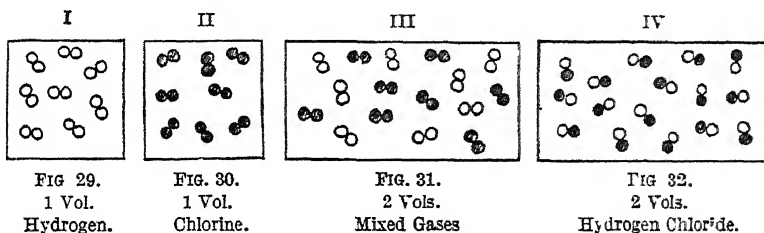
Represent the volumes by squares, the hydrogen atoms by white circles and the chlorine atoms by black circles.



Gay-Lussac thought that the gas particle might be the atom, and that equal volumes of gases might contain equal numbers of these particles. From our picture we see that one volume of hydrogen contains 8 atoms or particles (the number 8 is chosen for convenience in drawing the picture; the actual number of particles in one c.c. of gas is of the order of 10^{19} , a magnitude of which we can form no conception), the volume of chlorine contains the same, but the two volumes of hydrogen

chloride which should contain 16 particles only contain 8, therefore Gay-Lussac's guess must be wrong.

Avogadro's Hypothesis. In 1811, Avogadro, an Italian physician, propounded an important theory which gets over Gay-Lussac's difficulty by assuming that the particles of a gas are not single atoms but molecules, that is, clusters of atoms. Avogadro's Hypothesis is as follows: 'Equal volumes of all gases, at the same temperature and pressure, contain the same number of molecules.' Now draw the picture again, assuming that the molecules of hydrogen and chlorine each contain two atoms.



Square I represents 1 volume of hydrogen containing 8 molecules, each consisting of 2 atoms. Square II represents 1 volume of chlorine containing 8 molecules, also consisting each of 2 atoms. Double square III shows two volumes of the mixed gases before combination. If a light be applied, the hydrogen and chlorine unite with an explosion. The molecules are broken up, each white atom lays hold of a black one and we have 16 new molecules formed, each containing a white and a black atom, as in double square IV.

Assuming that Avogadro's hypothesis is correct, we can shew that the molecule of hydrogen and the molecule of chlorine must each consist of two atoms at least. Looking at our picture we see that from 1 volume of hydrogen containing 8 molecules, and 1 volume of chlorine containing 8 molecules, we obtain 2 volumes of hydrogen chloride containing sixteen molecules. Now each molecule of hydrogen chloride consists of a bit of hydrogen and a bit of chlorine, that is, the 16 molecules contain 16 bits of hydrogen which must have come from the 8 molecules of hydrogen, and 16 bits of chlorine which must have come from the 8 molecules of chlorine. Therefore as the atom cannot be subdivided, the 8 molecules of hydrogen and

the 8 molecules of chlorine must each consist of at least 2 atoms. In the same way it can be shewn that the molecules of oxygen and nitrogen contain 2 atoms each, assuming Avogadro's hypothesis to be correct.

Take next the union of hydrogen and oxygen to form water. Experiment has established that 2 volumes of hydrogen unite with 1 volume of oxygen to form water, which will be in the form of steam if the temperature of the mixed gases is kept at 100°C .

I

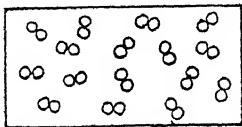


FIG. 33.
2 Vols.
Hydrogen.

II

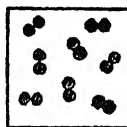


FIG. 34.
1 Vol.
Oxygen.

III

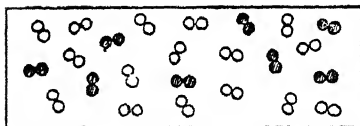


FIG. 35
3 Vols.
Mixed Gases.

IV

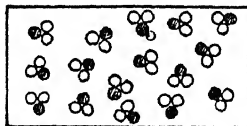


FIG. 36.
2 Vols.
Steam.

Double square I represents 2 volumes of hydrogen containing 16 molecules. Square II represents 1 volume of oxygen, containing 8 molecules. Triple square III shews 3 volumes of the mixed gases before combination. Double square IV shews 2 volumes of steam produced when the mixed gases have been exploded. In this case, each black oxygen atom seizes 2 white hydrogen atoms to form the new molecule of water.

QUESTIONS

1. Write a short account of Dalton's Atomic Theory and shew how it accounts for the facts summarised in the Law of Multiple Proportions. Two oxides of a metal M contain 79.89% and 88.83% of M respectively. Shew that these figures illustrate this Law.
(Scot. Univ. Entrance.)

2. What simple relationship has been found to exist between the volumes of gases which take part in a chemical change? Describe an experiment illustrating this. What volume of air containing 21% of oxygen would be needed for the complete combustion of 15 litres of acetylene? (London Matric.)

3. State Gay-Lussac's Law of Gaseous Volumes and illustrate it by two examples. A mixture of 75 c.c. of oxygen and 100 c.c. of carbon monoxide is ignited in a strong closed tube. After cooling the tube is opened over mercury. Describe the nature and amount of gas left in the tube, at the same temperature and pressure. Had strong caustic soda been used instead of mercury, what would have happened? (Scot. Univ. Entrance.)

4. What is the statement known as Avogadro's Law? Shew how it is used to determine the weights of gaseous molecules relative to the weight of the hydrogen molecule. (Scot. Univ. Entrance.)

CHAPTER X

ATOMIC WEIGHT. MOLECULAR WEIGHT. VAPOUR DENSITY. DIFFUSION

Atomic Weight. Dalton's theory states that atoms of different elements differ in weight. The actual weight of the hydrogen atom is 1.66×10^{-24} gram, and the weights of other atoms are of the same order of magnitude. It is obviously inconvenient then to use the absolute weights of the atoms in chemical calculations even if they had been all determined, which is not the case. Consequently, relative weights are made use of, and Dalton attempted to fix the relative weights of some of the atoms taking the weight of the atom of hydrogen, the lightest of the atoms, as unity. The atomic weight of an element may be defined as 'the number of times its atom is heavier than the hydrogen atom' or 'the ratio of the weight of its atom to the weight of an atom of hydrogen.' The equivalent weight in grams of an element is defined as the weight in grams which will combine with or replace one gram of hydrogen. In a few cases, one atom of an element combines with one atom of hydrogen or replaces one atom of hydrogen, and the atomic and equivalent weights (taking the weight of the atom of hydrogen as one gram) are the same. But more often, one atom of an element can replace 2, 3, 4 or more atoms of hydrogen, and the equivalent weight is $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$ of the atomic weight.

Molecular Weight. As the atomic weight is the weight of the atom, so the Molecular Weight is the weight of the molecule, and is found by adding together the weights of all the atoms of which it is composed.

Equal volumes of the same gas have the same weight, but equal volumes of different gases have different weights; thus, volume for volume, oxygen is 16 times heavier than hydrogen and carbon dioxide 22 times heavier. If equal volumes of all

gases, at the same temperature and pressure, contain the same number of molecules, the differences in weight must be due to differences in the weight of the various kinds of molecules; the molecule of oxygen weighs 16 times and the molecule of carbon dioxide 22 times as much as the hydrogen molecule. We can therefore find the relative weight of the molecule or the molecular weight of different gases by measuring the weights of equal volumes. In doing so it is convenient to take hydrogen as the standard.

Vapour Density. The Relative Density or Vapour Density of a gas is the number of times a given volume of it is heavier than an equal volume of hydrogen. To find the vapour density of a gas, weigh equal volumes of the gas and hydrogen; the ratio of these weights is the vapour density. For example:

1 litre of nitrogen weighs 1.251 grams,
and 1 litre of hydrogen weighs 0.09 gram;

\therefore the vapour density of nitrogen is $\frac{1.251}{0.09} = 14$.

In comparing vapour densities we take the density of hydrogen as 1. But the molecule of hydrogen contains 2 atoms and its molecular weight is 2. Therefore the molecular weight of hydrogen is twice its vapour density. This rule holds for all gases, that the molecular weight is twice the vapour density.

By definition,

$$\text{V.D.} = \frac{\text{Weight of given volume of gas}}{\text{Weight of same volume of hydrogen}}.$$

By Avogadro's hypothesis,

$$\text{V.D.} = \frac{\text{Weight of } x \text{ molecules of gas}}{\text{Weight of } x \text{ molecules of hydrogen}};$$

$$\therefore \text{V.D.} = \frac{\text{Weight of 1 molecule of gas}}{\text{Weight of 1 molecule of hydrogen}};$$

$$\therefore \text{V.D.} = \frac{\text{Molecular weight of gas}}{\text{Molecular weight of hydrogen}};$$

$$\therefore \text{V.D.} = \frac{\text{Molecular weight of gas}}{2}.$$

Hence the vapour density of a gas is half its molecular weight.

Determination of Vapour Density. EXPT.—To determine the vapour density of a volatile liquid, the Victor Meyer method is commonly used. This method

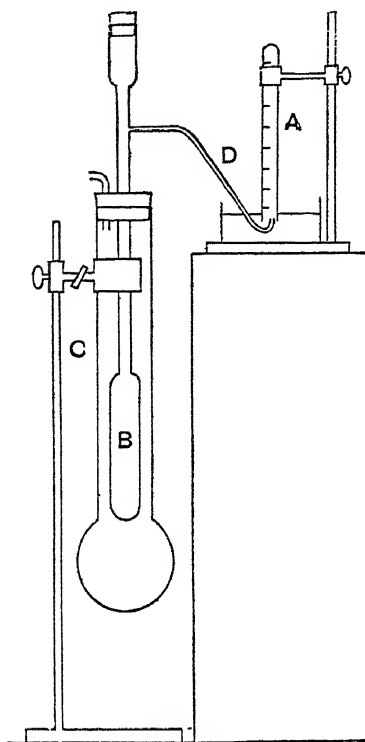


FIG 37 —Victor Meyer's Vapour Density Apparatus

measures the volume of air which is displaced by the vapour produced by a known weight of the substance. The inner vapour tube *B* is enlarged below into a cylindrical bulb, it is closed at the top with a cork, and a short distance below this it is connected with a bent capillary tube which dips under water in a pneumatic trough. Surrounding the inner tube is an outer tube *C* which serves as a heating jacket. In the bulb of this tube a liquid is placed which has a boiling point 20° – 30° higher than that of the volatile liquid. To make an estimation the inner tube *B* is thoroughly dried, the bulb of *C* half filled with liquid and the tubes fitted in position, a little asbestos or sand being placed in the bottom of inner tube *B*. The liquid whose vapour density is to be measured is then weighed out in a small stoppered bottle or glass bulb. The liquid in *C* is boiled until air ceases to bubble from the delivery tube *D*, the cork in *C* has openings to allow escape of vapour. The graduated tube *A* is then placed in position, the cork in *B* is re-

moved, the small bottle dropped in (the sand prevents fracture of the bulb), and the cork is quickly replaced. The liquid in the bottle is vaporised, the stopper forced out, and the vapour drives over into *A* its own volume of air. When no more bubbles pass over, the graduated tube is transferred to a cylinder of water, cooled and levelled. The volume of air is read, the temperature of the water and the barometric pressure noted, and the volume corrected accordingly. A correction is also made for the pressure of water vapour.

Calculation

Weight of liquid taken	= 0.09 gram.
Volume of gas	= 30 c.c.
Barometer reading	= 750 mm.
Temperature of water	= 20° C.
Vapour pressure of water at 20° C.	= 17.4 mm.

Subtracting the value of the vapour pressure of water from the barometer reading and reducing the volume of the gas to N.T.P., we get :

$$V = \frac{30 \times 732.6 \times 273}{293 \times 760} = 26.94 \text{ c.c.},$$

26.94 c.c. of vapour at N.T.P. weigh 0.09 gram,

1 c.c. of vapour at N.T.P. weighs $\frac{0.09}{26.94}$ gram,

1 c.c. of hydrogen at N.T.P. weighs 0.00009 gram ;

$$\therefore \text{V.D.} = \frac{0.09}{26.94 \times 0.00009} = 37.1,$$

and the molecular weight of the compound is 74.2.

Gram Molecular Volume. The word 'volume' as we have been using it, has only a relative meaning; it may be any quantity, a cubic foot, a litre, or any other measure of capacity. Instead of saying 'one volume of hydrogen unites with one volume of chlorine to form two volumes of hydrogen chloride,' we may say 'one cubic foot or one litre of hydrogen unites with one cubic foot or one litre of chlorine to form two cubic feet or two litres of hydrogen chloride.' A definite unit of volume has however been fixed, known as the **Gram Molecular Volume**. This is the volume occupied by 2 grams of hydrogen, measured at N.T.P. which is 22.4 litres. Now according to Avogadro's hypothesis, a molecule of hydrogen will occupy the same volume as a molecule of any other gas at the same temperature and pressure, so if the molecular weight of hydrogen in grams occupies a space of 22.4 litres, the molecular weight of every gas, in grams, will occupy the same volume. This volume of 22.4 litres is known as the gram molecular volume.

Diffusion. When a strongly scented flower or an open bottle of perfume is introduced into a room, we notice how quickly our sense of smell makes us aware of its presence. The scented particles are not necessarily carried by air currents, but have

their own independent power of motion. It can also be shewn that when two gases are brought together, they become thoroughly mixed in a very short time. Mixing is much slower between liquids, and is almost unobservable in the case of solids. This mixing of gases and liquids is known as Diffusion. Confining ourselves to gases, we find that each gas has its own rate of diffusion. Graham's law of diffusion states that the rate of diffusion is inversely proportional to the square root of the density of the gas.' Hydrogen, being the lightest gas, has the greatest speed of diffusion. Comparing hydrogen and oxygen :

Relative density of hydrogen = 1 and $\sqrt{1}=1$.

Relative density of oxygen = 16 and $\sqrt{16}=4$;

but the rates of diffusion are inversely proportional to the square roots of the densities, so

Rate of diffusion of hydrogen = 4.

Rate of diffusion of oxygen = 1.

Hydrogen thus diffuses 4 times as quickly as oxygen.

Expt.—To compare the speeds of diffusion of hydrogen and carbon dioxide with that of air. Fix on a retort stand a pot of porous unglazed earthenware as shown. An ordinary clay pipe will serve the purpose if the mouth of the bowl is stopped with a plug of plaster of Paris. The pot is connected with a length of glass tubing, the lower end of which dips into a coloured liquid. To show that hydrogen diffuses more rapidly than air, the apparatus is arranged as in Fig. 38. An inverted glass beaker covers the pot. A stream of gas is passed into the beaker from a hydrogen apparatus, thus surrounding the pot with an atmosphere of hydrogen. As hydrogen is lighter than air and diffuses more rapidly, it passes in through the material of the pot more quickly than the air can pass out, so the gas pressure inside the pot increases and bubbles of air pass through the liquid. In Fig. 39 a stream of carbon dioxide is led into the beaker and the contrary effect takes place. Carbon dioxide gas is heavier than air and diffuses more slowly, so the air passes out faster than the carbon dioxide can enter, and the gas pressure in the pot decreases, with the result that the liquid is sucked up into the tube.

Relative density of hydrogen = 1.

Relative density of air = 14.4.

Relative density of carbon dioxide = 22 ;

∴ the ratio of the rates of diffusion is

$$\frac{1}{\sqrt{1}} : \frac{1}{\sqrt{14.4}} : \frac{1}{\sqrt{22}} \quad \text{or} \quad 1 : \frac{1}{3.8} : \frac{1}{4.7}$$

Hydrogen therefore diffuses 3.8 times as rapidly as air, and 4.7 times as rapidly as carbon dioxide.

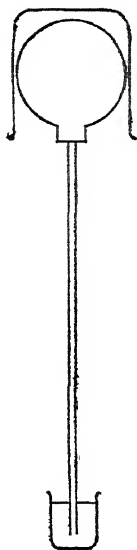


FIG. 38.

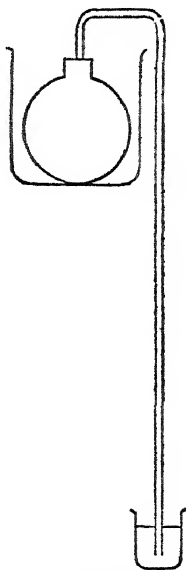


FIG. 39.

The explanation of the diffusion of gases is that the particles or molecules of a gas are in a state of constant motion in all directions. The hydrogen molecule is said to travel faster than a bullet from a gun. We should realise that a gas exercises pressure, and that this pressure is due to the continual bombardment of the walls of the vessel containing the gas by the swift-moving molecules. Referring back to our illustration of the effect of pressure upon a gas enclosed in a cylinder with an air-tight fitting piston: when the gas is compressed to half its volume the molecules strike the walls of the cylinder twice as frequently as before, so that the pressure of the gas is doubled. Remember that the pressure of the gas in the cylinder is

always resisting compression, and is equal to that on the piston, so that when we speak of pressure upon a gas we should keep in mind that the gas itself exercises an equal and opposite pressure. If a fuller explanation of this theory, known as 'the kinetic theory of gases,' is desired, a more advanced text-book should be consulted.

QUESTIONS

1. Explain the terms, atomic weight, equivalent weight. Describe in detail some method by which the equivalent weight of zinc might be determined. What other data would be required to determine the atomic weight?

(Oxford and Camb. School Cert.)

2. The chloride of a metal contains 88.6% of chlorine. Calculate the equivalent of the metal. When volatilised, 0.504 gram of chloride occupies 532 c.c. at a temperature of 819° C. and under a pressure of 800 mm. of mercury. Calculate the molecular weight of the compound.

(Scot. Leaving Cert.)

3. Describe a method by which the vapour density of chloroform could be determined.

(Oxford and Camb. School Cert.)

4. The oxide of an element contains 53% of the element and the vapour density of the chloride of the element is 66. Calculate (a) the atomic weight, (b) the valency of the element. Point out clearly what assumptions are made in the course of the calculations.

(London Matric.)

5. Explain the meaning of the term 'diffusion,' and describe experiments to shew that hydrogen diffuses more rapidly than air, and carbon dioxide more slowly. State Graham's Law of Diffusion.

CHAPTER XI

SYMBOLS. FORMULAE AND EQUATIONS. VALENCY. DETERMINATION OF ATOMIC WEIGHTS. DULONG AND PETIT'S LAW

Now let us collect some of the chemical reactions which we have studied, and put them into the form of algebraic equations, bearing in mind that we are dealing with definite quantities of real substances, not with mathematical symbols.

Mercuric oxide	gives mercury + oxygen.
Iron + sulphur	give ferrous sulphide.
Magnesium + oxygen	give magnesium oxide.
Mercury + iodine	give mercurous iodide.

This method of representing a chemical reaction is rather tedious and cumbrous, so that chemists instead of writing out the full names of substances have adopted a system of abbreviations.

About 90 elements are known. To each of these a **Symbol** has been assigned, which usually consists of one or two letters of its English or Latin name. Take the element iron. There are three other elements whose names begin with the letter I, iodine, iridium and indium. Iodine is represented by the symbol I, iridium by Ir, indium by In, and iron, to distinguish it from the other three, by Fe, the first two letters of its Latin name 'ferrum.' Following are the names and symbols of some of the commoner elements; a full list is given at the end of the book.

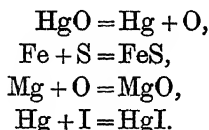
Aluminium	Al	Calcium	Ca
Antimony	Sb (Stibium)	Carbon	C
Arsenic	As	Chlorine	Cl
Barium	Ba	Chromium	Cr
Bismuth	Bi	Copper	Cu (Cuprum)
Boron	B	Gold	Au (Aurum)
Bromine	Br	Helium	He

Hydrogen	H	Oxygen	O
Iodine	I	Phosphorus	P
Iron	Fe (Ferrum)	Potassium	K (Kalium)
Lead	Pb (Plumbum)	Silver	Ag (Argentum)
Magnesium	Mg	Sodium	Na (Natrium)
Mercury	Hg (Hydrargyrum)	Sulphur	S
Nickel	Ni	Tin	Sn (Stannum)
Nitrogen	N	Zinc	Zn

The symbol represents one atom of the element and also a definite weight of that element known as the atomic weight. Any number of atoms greater than unity is indicated by a small figure placed immediately after, and slightly below the symbol. Thus H_2 means two atoms of hydrogen and O_3 three atoms of oxygen. The molecule is represented by a **Formula**. If it is the molecule of a compound, containing more than one kind of atom, the symbols of the atoms of which it is composed are written side by side, small figures being added after them if necessary, to show the number of atoms. A larger figure in front of the formula indicates the number of molecules. Some examples of formulae are :

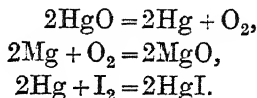
- HgO represents 1 molecule of mercuric oxide, containing 1 atom of mercury and 1 atom of oxygen.
 $2FeS$ represents 2 molecules of ferrous sulphide, each molecule containing 1 atom of iron and 1 atom of sulphur.
 $HgCl_2$ represents 1 molecule of mercuric chloride, containing 1 atom of mercury and 2 atoms of chlorine.
 $2KClO_3$ represents 2 molecules of potassium chlorate, each molecule containing 1 atom of potassium, 1 atom of chlorine and 3 atoms of oxygen.
 $3O_2$ represents 3 molecules of oxygen, each molecule containing 2 atoms of oxygen.

Let us now re-write the Equations already given, using symbols and formulae :



It has been said that the molecule is the smallest weight in which the original properties of the substance are retained. In an equation a substance must therefore be represented by its molecule. We have written an atom of oxygen and an atom of iodine, but as it is known that the molecules of the elements

Oxygen, Hydrogen, Nitrogen, Fluorine, Chlorine, Bromine and Iodine each contain two atoms, *e.g.* O_2 and I_2 , it is more correct to double the quantities in the equations and write them as follows :



It is customary to represent the molecule of all other elements than the above simply by the symbol, *e.g.* Fe and S, as if it consisted of only one atom, for the following reasons : a doubt may exist as to the number of atoms in the molecule, or the number may vary at different temperatures.

Valency. Most of the elements unite with oxygen to form oxides, but they do not all unite with it in the same atomic proportions. The following are the formulae of some oxides :

Sodium oxide	-	-	-	-	Na_2O
Magnesium oxide	-	-	-	-	MgO
Sulphur dioxide	-	-	-	-	SO_2
Ferric oxide	-	-	-	-	Fe_2O_3
Phosphoric oxide	-	-	-	-	P_2O_5

Also, in accordance with the law of multiple proportions, some of the elements can form more than one oxide. For example, sulphur forms sulphur dioxide SO_2 and sulphur trioxide SO_3 . Now these are not haphazard combinations, but depend on the combining power or valency of the respective elements.

Let us suppose that every atom is provided with a certain number of 'hooks,' which are of course purely imaginary, and that each of these hooks can grapple one hook of another atom and so unite with it. These imaginary hooks are called in chemical language 'bonds,' and the bonds are shown in another kind of formula which is frequently employed, the graphic 'formula.

	Ordinary formula.	Graphic formula
Sodium oxide	Na_2O	$\begin{array}{c} Na \\ \diagup \\ Na \end{array} O$
Magnesium oxide	MgO	$Mg = O$
Sulphur dioxide	SO_2	$\begin{array}{c} O \\ // \\ S \\ \backslash \\ O \end{array}$

	Ordinary formula	Graphic formula.
Sulphur trioxide	SO_3	$\begin{array}{c} \text{O} \\ // \\ \text{O}=\text{S} \\ // \\ \text{O} \end{array}$
Phosphorus pentoxide	P_2O_5	$\begin{array}{c} \text{O} \quad \text{O} \\ // \quad // \\ \text{O}=\text{P}-\text{O}-\text{P}=\text{O} \\ // \quad // \\ \text{O} \quad \text{O} \end{array}$
Phosphorus trioxide	P_2O_3	$\text{O}=\text{P}-\text{O}-\text{P}=\text{O}$

The oxygen atom has 2 hooks and lays hold of 2 atoms of sodium, each of which has only 1 hook. Magnesium has 2 hooks and consequently grapples the 2 hooks of 1 atom of oxygen. The sulphur atom is provided with 6 hooks, and can hold 2 or 3 atoms of oxygen. In sulphur dioxide it holds 2, and 2 hooks are not used; in sulphur trioxide all six hooks are used. Phosphorus has 5 hooks. If the 5 are all employed, 2 atoms of phosphorus can hold 5 atoms of oxygen (10 hooks hold 10 hooks), if only 3 are used, the oxide produced is phosphorus trioxide or phosphorous oxide, P_2O_3 .

The names 'monoxide,' 'dioxide,' 'trioxide,' 'tetroxide,' and 'pentoxide' are applied to oxides containing respectively 1, 2, 3, 4, and 5 atoms of oxygen.

This 'hook' theory is not of course confined to oxides, but holds for all compounds. An atom may not use all its hooks, in which case the resulting molecule has still some combining power. The number of hooks made use of by one atom of an element is the **Valency** of the element. Valency is shewn by prefixes similar to those already given. A monovalent atom has 1 hook, a divalent atom 2, a trivalent atom 3, a tetravalent atom 4, a pentavalent atom 5, and a hexavalent atom 6 hooks. The valency of hydrogen is 1, so the valency of an element is commonly defined as 'the number of hydrogen atoms which one atom of the element can combine with or replace.' From our definition of an equivalent, we can also deduce the relationship, $\text{valency} = \frac{\text{atomic weight}}{\text{equivalent weight}}$, thus :

At. wt. of magnesium = 24, Eq. wt. = 12 ; \therefore Valency = $\frac{24}{12} = 2$.

At. wt. of aluminium = 27, Eq. wt. = 9 ; \therefore Valency = $\frac{27}{9} = 3$.

For Table of Valencies, see p. 127.

Determination of Atomic Weight. We have up to now been using for simplicity Dalton's standard of atomic weights, hydrogen = 1, but the standard now generally adopted is oxygen = 16. The chief reason for this preference is as follows. The atomic weight of an element is determined by the analysis of compounds in which it is contained, preferably compounds of the element with the standard. Now oxygen forms oxides with almost all elements, while hydrogen forms few compounds with metals. Oxygen thus affords a far greater range of compounds from which atomic weights may be established. The atomic weights given in this book are on the oxygen standard. The exact atomic weight of hydrogen becomes on this standard 1.008, but the figure 1 is used for calculations when extreme accuracy is not required.

Avogadro's hypothesis may be applied to the determination of atomic weights. If we take a number of different compounds containing a particular element, it is very probable that the molecule of at least one of them will contain only one atom of the element. When an element forms several volatile compounds, the molecular weights of these can be determined by measuring their vapour densities. Then, by analysis, the weight of the element contained in each molecular weight is estimated, and the smallest weight found is taken as the weight of one atom or the atomic weight. The atomic weight may be thus defined as 'the smallest weight of an element found in a molecular weight of any of its compounds.' This is illustrated in the following table.

	Molecular Weight	Weight of Element contained in the Molecule					
		Hydrogen	Oxygen	Carbon	Chlorine	Sulphur	Formula
Hydrogen chloride	36.468	1.008			35.46		HCl
Chlorine peroxide	67.46		32		35.46		ClO ₂
Carbon monoxide	28.00		16	12			CO
Carbon dioxide	44.00		32	12			CO ₂
Hydrogen sulphide	34.08	2.016				32.064	H ₂ S
Sulphur dioxide	64.064		32			32.064	SO ₂
Water	18.016	2.016	16				H ₂ O
Acetylene	26.016	2.016		24			C ₂ H ₂
Sulphur chloride	135.048				70.92	64.128	S ₂ Cl ₂
Propane	44.064	8.064		36			C ₃ H ₈

Note that in each case the smallest weight of an element contained in any molecule is taken as the atomic weight, and that the other weights of the same element are simple multiples of the atomic weight. Also observe how the construction of the formula follows naturally from these considerations.

Dulong and Petit's Law. The method of determining atomic weights just described is not applicable to all elements, as many of them do not form volatile compounds suitable for vapour density measurements. To find the atomic weight of such an element, we can measure its equivalent weight by one of the methods already given, the atomic weight is then either equal to or a small multiple of this value. **Dulong and Petit's Law**, published by its discoverers in 1819, is invaluable in deciding which of several possible values is the true atomic weight. It is only applicable to solid elements. The law states that 'the atomic weight of a solid element multiplied by its specific heat gives nearly the same value in every case.' This product, known as the **Atomic Heat**, is approximately equal to 6.3. As examples of the use of the law, take the following :

What is the atomic weight of copper ? We have measured the equivalent weight and find it to be 31.8. Is this value or a multiple of it the atomic weight ?

The specific heat of copper is 0.0923,

atomic weight $\times 0.0923 = 6.3$,

$$\text{or} \quad \text{atomic weight} = \frac{6.3}{0.0923} = 67,$$

which is sufficiently near the mark to show that the correct atomic weight is $31.8 \times 2 = 63.6$, and that the copper atom is divalent.

Take another example :

0.5 gram of aluminium gave with hydrochloric acid 622 c.c. of hydrogen at N.T.P.

1000 c.c. of hydrogen weigh 0.09 gram ; \therefore 622 c.c. weigh 0.056 gram, so 0.056 gram of hydrogen is replaced by 0.5 gram of aluminium ; \therefore 1 gram of hydrogen is replaced by

$\frac{0.5}{0.056} = 9$ grams of aluminium ; \therefore the equivalent of aluminium is 9.

The atomic weight must then be 9 or a multiple of 9.

The specific heat of aluminium is 0.2143;

$$\therefore \text{the atomic weight} = \frac{6.3}{0.2143} = 29,$$

$$\text{now valency} = \frac{\text{atomic weight}}{\text{equivalent weight}} = \frac{29}{9} = 3 \text{ approximately,}$$

and equivalent \times valency = atomic weight; $\therefore 9 \times 3 = 27$.

It should be borne in mind that Dulong and Petit's law is not sufficiently accurate to be used in determining atomic weights directly, but is valuable as a means of deciding which of several possible atomic weights is the correct one.

QUESTIONS

1. What is meant by the term 'valency'? How is the valency (a) of an element, (b) of a radical, determined? What valency is ascribed to (a) chlorine, (b) SO_4 ?

(Oxford and Camb. School Cert.)

2. Distinguish between the chemical equivalent and the atomic weight of an element, illustrating your answer by reference to any suitable metallic element. In an experiment, 0.49 gram of a metal when dissolved in hydrochloric acid displaced 295 c.c. of dry hydrogen at 22°C . and 752 mm. pressure. The specific heat of the metal was 0.152. Calculate the chemical equivalent and the atomic weight of the metal.

(Scot. Leaving Cert.)

3. What is the relationship between specific heat and atomic weight? The specific heat of a metal is 0.031, and 3.09 grams gave 3.33 grams of the oxide. Calculate the approximate atomic weight of the metal from these data.

(Scot. Univ. Entrance.)

4. 1.5 grams of a metal whose valency is known to be 3 gave 1.8 grams of oxide when completely oxidised. Find (a) the equivalent weight of the metal, (b) its atomic weight, (c) its specific heat.

(Scot. Leaving Cert.)

5. What is the valency of sulphur in hydrogen sulphide, of nitrogen in ammonia, of carbon in carbon dioxide? Write structural formulae for carbonic acid, potassium nitrate, and potassium hydrogen sulphate.

(Scot. Univ. Entrance.)

CHAPTER XII

CALCULATIONS INVOLVING FORMULAE AND EQUATIONS

Information given by a Formula. The formula represents one molecule of a substance and gives the following information.

1. The elements contained in the substance.
2. The relative weights of these elements contained in the molecule.

3. The molecular weight of the substance.

4. If the substance is a gas, or can be converted into a gas by heating, the molecular weight in grams in the gaseous state will occupy a volume of 22.4 litres at N.T.P. Consequently, we can say that the molecular formula of a gas represents a volume of 22.4 litres when the weights of its component atoms are stated in grams. Thus CO_2 , CO , O_2 , NH_3 , H_2 are all molecular formulae of gases, and when they occur in an equation in which the weights are stated in grams, each of these formulae represents a volume of 22.4 litres at N.T.P.

Example. Calcium carbonate, CaCO_3 . Looking up the table of symbols and atomic weights, we find that CaCO_3 contains 1 atom of calcium, 1 atom of carbon, and 3 atoms of oxygen, and that the atomic weights are, calcium = 40, carbon = 12, oxygen = 16. The weights of these elements contained in the molecule are found by multiplying the atomic weight of each element by the number of atoms, and the molecular weight is the sum of the weights of all the atoms in the molecule.

Formula.	Weight of Atoms.	Total.
Ca	= 40 × 1	= 40
C	= 12 × 1	= 12
O ₃	= 16 × 3	= 48
Molecular weight =		<u>100</u>

Example. Carbon dioxide, CO_2 . Atomic weights, carbon = 12, oxygen = 16.

Formula.	Weight of Atoms	Total
C	= 12 \times 1	= 12
O ₂	= 16 \times 2	= <u>32</u>
	Molecular weight =	<u>44</u>

and

Volume at N.T.P. = 22.4 litres.

Example. Water, H_2O . Atomic weights, H = 1, O = 16. Water is converted into steam by heating. Steam when cooled condenses into water, which at N.T.P., that is, at 0°C ., becomes ice. Steam cannot therefore be measured at 0°C ., but the volume which 18 grams would theoretically occupy at N.T.P. is found by calculation to be 22.4 litres.

Formula	Weight of Atoms	Total
H ₂	= 1 \times 2	= 2
O	= 16 \times 1	= <u>16</u>
	Molecular weight =	<u>18</u>

and volume in the gaseous state at N.T.P. = 22.4 litres.

Calculation of Percentage Composition. To calculate the percentage composition of a substance, given its formula and the atomic weights of the elements contained in it.

Example. Calculate the percentage composition of potassium nitrate, KNO_3 . The atomic weights are, K = 39, N = 14, O = 16.

Formula.	Weight of Atoms	Total
K	= 39 \times 1	= 39
N	= 14 \times 1	= 14
O ₃	= 16 \times 3	= <u>48</u>
	Molecular weight =	<u>101</u>

$$\text{Percentage of potassium} = \frac{39 \times 100}{101} = 38.61$$

$$\text{Percentage of nitrogen} = \frac{14 \times 100}{101} = 13.86$$

$$\text{Percentage of oxygen} = \frac{48 \times 100}{101} = 47.53$$

100.00

Example. Calculate the percentage composition of ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$. Atomic weights, Fe = 56, S = 32, O = 16.

Formula.	Weight of Atoms.	Total.
Fe_2	= 56×2	= 112
S_3	= 32×3	= 96
O_{12}	= 16×12	= 192
Molecular weight =		<u>400</u>
Percentage of iron	= $\frac{112 \times 100}{400}$	= 28
Percentage of sulphur	= $\frac{96 \times 100}{400}$	= 24
Percentage of oxygen	= $\frac{192 \times 100}{400}$	= <u>48</u>
		<u>100</u>

Calculation of the Empirical Formula from the Percentage Composition. The 'empirical formula' of a compound means the simplest formula which can be calculated from the percentage composition. The 'molecular formula' represents that weight in grams of the substance which in the state of vapour would occupy the 'gram molecular volume,' 22.4 litres. The elements in a molecular formula are not always in the simplest ratio. For example, the formula of acetylene is C_2H_2 . The simplest formula would be CH, but $\text{C}_2\text{H}_2 = 26$ is the number of grams of acetylene which at N.T.P. occupies the volume of 22.4 litres. When it is impossible to determine the true molecular formula, the empirical formula is used, and is calculated as follows.

The composition of a substance is the same as that of its molecule, therefore the percentage composition of a substance shews the proportions by weight of the elements in the molecule. If we divide a given weight of an element by the weight of its atom, the quotient gives the number of atoms of the element in the given weight. Therefore if we divide the percentage of each element by its atomic weight, we get the proportions by number of the atoms in the molecule. If these proportions are not whole numbers (we cannot have fractions of an atom in a molecule), they must be reduced to the smallest possible whole numbers. Divide each of these numbers by the

smallest of them, the smallest then becomes 1 atom and the others become multiples of 1 atom. An example or two will explain this better.

Example. A compound on analysis gave the following results.

Magnesium = 60%,

Oxygen = 40%.

Divide the percentage of each element by its atomic weight, magnesium = 24, oxygen = 16.

Magnesium = $\frac{60}{24} = 2.5$,

Oxygen = $\frac{40}{16} = 2.5$;

\therefore number of Mg atoms : number of O atoms :: 2.5 : 2.5.

The number of Mg atoms evidently = the number of O atoms, and the simplest formula will contain $\frac{2.5}{2.5}$ or 1 atom of each.

The formula is therefore MgO, magnesium oxide.

Example. A compound on analysis gave the following results.

Sodium = 32.39%,

Sulphur = 22.53%,

Oxygen = 45.08%.

Divide the percentage of each element by its atomic weight, sodium = 23, sulphur = 32, oxygen = 16.

Sodium = $\frac{32.39}{23} = 1.408$,

Sulphur = $\frac{22.53}{32} = 0.704$,

Oxygen = $\frac{45.08}{16} = 2.817$;

\therefore No. of Na atoms : No. of S atoms : No. of O atoms =
1.408 : 0.704 : 2.817

If we then divide each of these numbers by the smallest, 0.704, the proportion becomes $\frac{1.408}{0.704} : \frac{0.704}{0.704} : \frac{2.817}{0.704} = 2 : 1 : 4$.

The proportion by number of the atoms in the molecule is then 2 : 1 : 4 and the formula is Na₂SO₄, sodium sulphate.

Example. A compound on analysis gave these results.

Potassium = 24.69%,

Manganese = 34.81%,

Oxygen = 40.50%.

Divide the percentage of each element by its atomic weight, potassium = 39, manganese = 55, oxygen = 16.

$$\text{Potassium} = \frac{24.69}{39} = 0.633,$$

$$\text{Manganese} = \frac{34.81}{55} = 0.633,$$

$$\text{Oxygen} = \frac{40.50}{16} = 2.53;$$

∴ No. of K atoms : No. of Mn atoms : No. of O atoms =
0.633 : 0.633 : 2.53

Dividing each of these numbers by the smallest, 0.633, the proportion becomes $\frac{0.633}{0.633} : \frac{0.633}{0.633} : \frac{2.53}{0.633} = 1 : 1 : 4$.

The proportion by number of the atoms in the molecule is then 1 : 1 : 4, and the formula is KMnO_4 , potassium permanganate.

Example. A compound on analysis gave these results.

Potassium = 26.53%,

Chromium = 35.37%,

Oxygen = 38.10%.

Divide the percentage of each element by its atomic weight, K = 39, Cr = 52, O = 16

$$\text{Potassium} = \frac{26.53}{39} = 0.68,$$

$$\text{Chromium} = \frac{35.37}{52} = 0.68,$$

$$\text{Oxygen} = \frac{38.10}{16} = 2.38;$$

∴ No. of K atoms : No. of Cr atoms : No. of O atoms =
0.68 : 0.68 : 2.38

Dividing each of these numbers by the smallest, 0.68, the proportion becomes $\frac{0.68}{0.68} : \frac{0.68}{0.68} : \frac{2.38}{0.68} = 1 : 1 : 3.5$.

In this case we still have a fraction, which is inadmissible, so we must convert the atomic proportions into the smallest whole numbers by multiplying by a factor.

Multiplying by 2, we get 2 : 2 : 7, which is the ratio of the numbers of the atoms in the molecule, and the formula is $K_2Cr_2O_7$, potassium dichromate.

Example. A compound on analysis gave these results.

Sodium = 18.54%,

Sulphur = 25.81%,

Oxygen = 19.36%,

Water = 36.29%.

The water is water of crystallisation, and when the percentage of water is divided by its molecular weight, the quotient gives the number of molecules of water. Divide as usual the percentage of each element by its atomic weight, Na = 23, S = 32, O = 16, molecular weight of water = 18.

$$\text{Sodium} = \frac{18.54}{23} = 0.8,$$

$$\text{Sulphur} = \frac{25.81}{32} = 0.8,$$

$$\text{Oxygen} = \frac{19.36}{16} = 1.2,$$

$$\text{Water} = \frac{36.29}{18} = 2.0;$$

$$\therefore \text{Na atoms : S atoms : O atoms : Water molecules} = \\ 0.8 : 0.8 : 1.2 : 2.0$$

Dividing each of these by the smallest, 0.8, the proportions become $\frac{0.8}{0.8} : \frac{0.8}{0.8} : \frac{1.2}{0.8} : \frac{2.0}{0.8} = 1 : 1 : 1.5 : 2.5$.

In this case also, we still have fractions, so we must multiply by the smallest factor which will convert the atomic proportions into whole numbers. Multiplying by 2, we get 2 : 2 : 3 : 5, which is the ratio required, and the formula is $Na_2S_2O_3 \cdot 5H_2O$, sodium thiosulphate. The water of crystallisation is given as molecules, not as atoms.

Calculations by Use of Equations

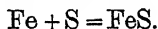
What information do we obtain from a chemical equation ?

1. It represents a chemical reaction, and shews the reacting substances and the products formed.
2. It tells us the exact relative weights of the reacting substances and of the products.
3. It tells us the volumes of any gases which take part in the reaction.

What information do we *not* obtain from a chemical equation ?

1. It does not always tell us whether the reacting substances and products are in the gaseous, liquid, or solid state.
2. It does not tell us whether the reaction proceeds at the ordinary temperature or requires heat for its completion.
3. It does not tell us whether the reaction takes place quickly or slowly.

Example. Take as an example the equation for the reaction which we have used already as a method of making a compound. What do we learn from it ?

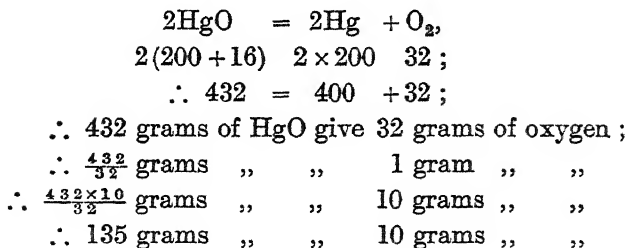


1. We learn that when iron and sulphur combine, they form ferrous sulphide.
2. As the atomic weight of iron is 56 and the atomic weight of sulphur is 32, we learn that 56 parts by weight of iron unite with 32 parts of sulphur to produce 88 parts of ferrous sulphide.

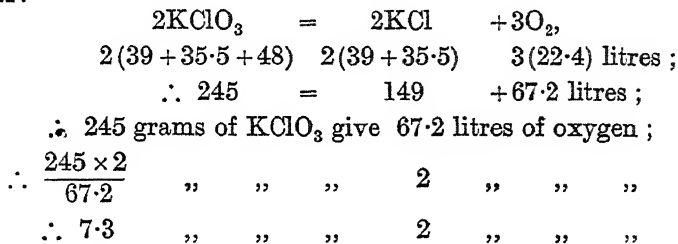
But the equation does not tell us the conditions required for the union of iron and sulphur. The two solid elements may be mixed, but shew no sign of combination at ordinary temperatures. The mixture requires the application of heat. Again, solid sulphur might be added to molten iron, or iron might be heated in sulphur vapour. The equation gives us no information on these points. In answering examination questions, do not be satisfied with writing a bare equation, but describe as far as possible the necessary conditions for the reaction.

Example of Calculation. What weight of mercuric oxide will give 10 grams of oxygen ? Atomic weights, Hg 200, O 16.

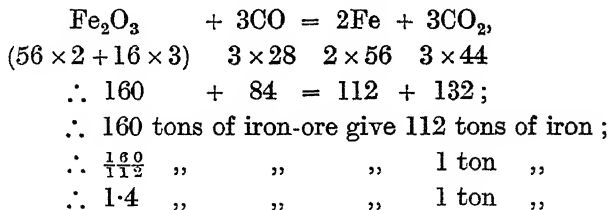
Write down the weights of each substance under the equation, thus :



Example. How much potassium chlorate is required to produce 2 litres of oxygen? The atomic weights are K = 39, Cl = 35.5, O = 16, and O₂ represents a volume of 22.4 litres at N.T.P.



Example. Iron ore (ferric oxide, Fe₂O₃) is reduced to metallic iron by carbon monoxide gas. How much iron ore is required to produce 1 ton of iron? The atomic weights are Fe = 56, C = 12, O = 16, and the equation is



Note that in this example where the quantities are stated in tons, not in grams, 3CO and 3CO₂ do not represent 3 × 22.4 litres. To find the volume of each gas, multiply 3 × 22.4 litres by the number of grams in a ton.

QUESTIONS

1. In the combustion of an organic substance it was found that 0.25 grams gave 0.293 grams of carbon dioxide and 0.09 grams of water. Find the simplest formula for the substance.

(Oxford and Camb. School Cert.)

2. Calculate the relative weights of mercuric oxide and potassium chloride which must be used in order to obtain equal volumes of oxygen under the same conditions of temperature and pressure. Describe, in detail, an experiment by which you could ascertain the percentage composition of mercuric oxide and the weight of one litre of oxygen at the temperature and pressure existing in the laboratory.

(London Matric.)

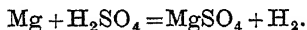
3. The gaseous oxide of an element contains 53.25% of oxygen, and 770 c.c. of the gas at N.T.P. weigh 1.031 grams. Find a formula for the gas from these data.

(Oxford and Camb. School Cert.)

4. What is the difference between empirical and molecular formula? What observations are required for fixing an empirical formula and what further information is necessary in order to assign a molecular formula?

(Scot. Univ. Entrance.)

5. Make a list of all the information you can derive from the equation,



(Scot. Leaving Cert.)

6. Describe in detail a method for finding the molecular weight of a volatile compound, *e.g.* benzene (B.P. 80°C). The percentage composition of a volatile liquid was found to be as follows: carbon 64.9%, hydrogen 13.5%, oxygen 21.6%. If 0.1146 gram of this liquid gave 36.3 c.c. of vapour at 11°C . and 752 mm. pressure, find its molecular weight and its formula.

(Scot. Leaving Cert.)

7. Manganese chloride is found on analysis to contain, manganese 43.63%, chlorine 56.36%. Calculate its simplest formula. (Mn = 55, Cl = 35.5.)

(London Matric.)

CHAPTER XIII

HYDROGEN

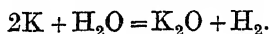
WE have already discovered in studying equivalents, that some metals displace hydrogen gas from dilute hydrochloric and sulphuric acids. This action of acids upon metals has been known from very early times. Van Helmont (1648) describes a gas obtained by the action of dilute sulphuric acid upon iron, and states that it is inflammable and does not support combustion. It was known to the chemists of the seventeenth and eighteenth centuries as 'inflammable air,' but was confused by them with other gases such as carbon monoxide and hydrogen sulphide, to which the term 'inflammable air' was also applied. H. Cavendish (1766) was the first to investigate the properties of hydrogen. He found that it produced water vapour when burned in air, and shewed that it was a distinct chemical substance. The name hydrogen or 'water producer' is due to Lavoisier.

Occurrence. Hydrogen is a colourless gas without taste or smell, and is the lightest of all known gases. It is not present in the atmosphere in any appreciable quantity, but is found in combination with other elements in the crust of the earth, of which it forms 1% by weight. Both hydrogen and oxygen are important constituents of vegetable and animal tissue. Water contains $\frac{1}{8}$ of its weight of hydrogen, and we can readily obtain the gas from water by several different methods. We have seen that oxygen combines with most elements, and some of the metals in particular have such a powerful affinity for oxygen that they extract it from water and thus set free hydrogen.

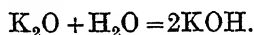
Preparation of Hydrogen. NOTE.—*As already explained on p. 35, the following experiments with potassium and sodium if considered unsafe may be omitted.*

EXPT.—Half fill a large trough or porcelain basin with water. Cut off a piece of potassium the size of a small pea. *If the metal is handled the fingers must be perfectly dry.* Note how the brilliant metallic lustre soon becomes dulled, owing to the formation of a film of potassium oxide, K_2O . Throw the piece of metal on the surface of the water, *and stand well back from it.* Observe that the potassium melts and seems to take fire, burning with a lilac-coloured flame, and giving out a hissing sound due to the formation of steam. At the end of the reaction there is an explosion caused by the molten caustic potash coming in contact with the water (from which it had been separated by a cushion of hydrogen) and generating a quantity of steam. *The face should be protected, as the particles of caustic potash fly in all directions, and if they come in contact with the skin may cause burns.*

The potassium has combined with the oxygen of the water to form potassium oxide, and hydrogen gas has been set free



The heat given out in the reaction is sufficient to ignite the hydrogen. It is the hydrogen then which burns, but the colour of the flame is due to the vapour of potassium. The oxide formed is a basic oxide and unites with the water giving potassium hydroxide, an alkali :



The solution should therefore be alkaline, but as prepared in the last experiment is probably too dilute to react with litmus paper.

EXPT.—Take a 5-inch porcelain basin half filled with water, and drop in one or two small pieces of potassium. When the reaction is over test the liquid with red litmus paper.

Repeat the last two experiments with metallic sodium, floating the metal on a piece of filter paper. The hydrogen takes fire and burns with a yellow flame due to sodium vapour. If filter paper is not used, the hydrogen does not take fire and may be ignited with a burning taper. The action is not so vigorous in this case, but an explosion takes place at the end of the reaction, and *the same precautions must be observed.*

EXPT.—To collect the hydrogen evolved. Wrap a piece of sodium in wire gauze or lead foil, in the latter case leaving a small opening so that the sodium may come in contact with the water. Drop the pellet into the pneumatic trough and place a test tube or

jar filled with water over the escaping gas. When the action ceases, cover the tube or jar with the thumb or with a greased plate. Invert the tube, uncover it and at the same instant light the gas with a taper, it burns with a bluish flame.

Some metals cannot decompose water at the ordinary temperature, but can decompose water at $100^{\circ}\text{C}.$, that is, steam.

EXPT.—To obtain hydrogen by heating magnesium in steam. Place a small bundle of magnesium ribbon in a hard glass tube. Connect to one end by a piece of rubber tubing a flask half full of water, placed on a wire gauze supported by a tripod. The other end is connected by a glass leading tube with a pneumatic trough, which contains a jar to receive the hydrogen. Disconnect the flask and heat it until the water is boiling freely. Warm the combustion tube to prevent water condensing in it. Then connect up the flask and heat the magnesium to a red heat. It burns, forming magnesium oxide. The hydrogen collects in the jar and can be tested with a lighted taper.

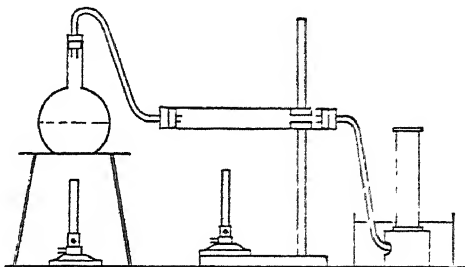
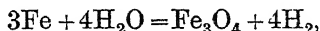
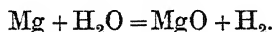


FIG 40.

Zinc dust or bright iron turnings can be substituted for magnesium in this experiment, and an iron tube may be used instead of a glass one. The equation for the action of iron on steam is



and that for the action of magnesium on steam is



Compare the magnesium oxide left in the tube with that obtained by burning in oxygen or air, place it on a piece of moist litmus paper. It is the same substance.

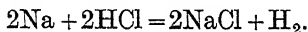
There is an easier method of obtaining hydrogen than by separating it from water or steam by means of a metal. We have already seen that a metal may be soluble in one or more acids, and hydrogen is frequently given off during the process. The acid usually employed is either dilute hydrochloric or

dilute sulphuric. Nitric acid and sulphuric acid, especially when concentrated, are, as we shall see later, oxidizing acids, and may give up oxygen to the hydrogen, converting it into water. Dilute nitric acid gives hydrogen with only two or three metals, *e.g.* magnesium and manganese. For the metal, zinc is the one commonly used, because it is easily acted upon, because it can be obtained fairly pure, and because it is cheap. Magnesium and iron would displace hydrogen from acids equally easily, but magnesium is too expensive and iron is difficult to obtain pure.

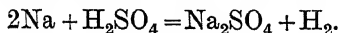
EXPT.—Take a small piece of granulated zinc in a test tube, and add some dilute hydrochloric acid. Note the effervescence due to evolution of hydrogen. Apply a lighted taper to the mouth of the tube : if there is any air mixed with it, the hydrogen will take fire with a slight explosion ; if the air has been expelled, it will burn quietly.

In the same way test the action of dilute hydrochloric, sulphuric, and nitric acids upon magnesium, iron, tin and copper. Tabulate your results, shewing the solubility of each metal in the three acids, both hot and cold ; this may be roughly judged by the amount of effervescence. Note the evolution of hydrogen or any other gas.

We have already considered the solution of salts, *e.g.* sodium chloride and potassium nitrate, in water. From these solutions the salt can be obtained unchanged by evaporation to dryness. The solution of a metal in an acid is not so simple, as it includes a chemical reaction. On evaporation the metal is not recovered, but an entirely different substance, a salt. The action of an acid on a metal is then one method of making a salt. For example, sodium with hydrochloric acid gives sodium chloride and hydrogen :



With sulphuric acid it gives sodium sulphate and hydrogen :



EXPT.—To make sodium chloride by the action of hydrochloric acid on sodium. Pour some dilute hydrochloric acid into a porcelain basin and cover it with a clock glass. Take a little sodium and cut it into very small pieces. Add these one by one to the acid, keeping the basin covered between additions. When the sodium is all dissolved evaporate the solution to dryness. The white residue is sodium chloride or common salt. Taste it.

This experiment may be performed quantitatively, taking 0.2-0.5 gram of sodium, and will serve to estimate the equivalent of sodium, taking chlorine as 35.5.

EXPT.—To prepare hydrogen from zinc and hydrochloric acid. Fit a half litre flask with a two hole rubber stopper. Insert a thistle funnel tube extending to the bottom of the flask, and a delivery tube to connect with a pneumatic trough. Remove the stopper, put some granulated zinc in the flask and replace the stopper and tubes, arranging the apparatus as shown. Then pour dilute hydrochloric acid into the funnel till the zinc and the end of the tube are well covered. Place a

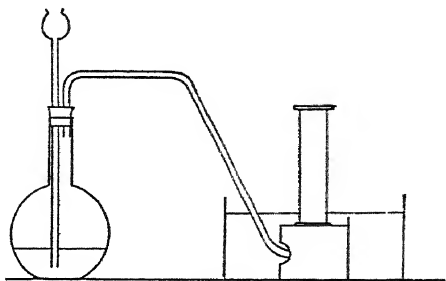
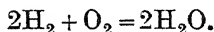


FIG. 41.

small jar full of water in the trough to collect the gas. Test the first two or three jars filled with a lighted taper. If the hydrogen is mixed with air there will be a slight explosion. When one burns quietly, then collect four jars and cover them with greased glass covers.

EXPT.—Invert one jar, remove the cover and immediately plunge into it a lighted taper. The hydrogen ignites and the taper is extinguished. This shows that hydrogen is combustible but does not support combustion. Compare this with the behaviour of oxygen.

The burning of hydrogen, that is, the union of hydrogen with oxygen, produces water; water is therefore an oxide of hydrogen:



EXPT.—Hold a dry cold beaker for a second or two over a Bunsen flame, and notice that it becomes covered with dew. This is condensed from the steam produced by the burning hydrogen, of which coal gas contains 50%.

EXPT.—Stand a second jar on the bench, mouth upwards, remove the cover and in a few seconds apply a lighted taper. There is no flame or explosion, as the hydrogen has disappeared. Take another jar of hydrogen, fix it in a clamp on a retort stand, mouth

downwards, keeping the cover in place during the operation. Remove the cover and in a few seconds apply a light. A flame shows that the gas is still there.

EXPT.—Take a fourth covered jar and hold it horizontally with its lip directly under the mouth of the empty jar in the retort stand. Gradually remove the cover to permit the gas to flow upwards, and when it has collected in the upper jar, test with a light.

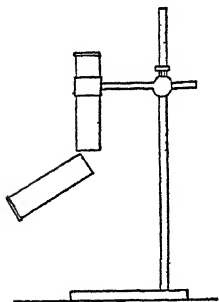


FIG 42.

This experiment may be varied by hanging an inverted beaker above one pan of a balance, and counterpoising it, that is, adding weights to the other pan until it is exactly balanced. Hydrogen is then poured up into the beaker and that end of the scale slowly rises.

A soap bubble may be blown, or a small collodion balloon inflated with hydrogen; when set free they rise very rapidly.

Properties. These experiments illustrate the lightness of hydrogen, and on account of this property it is used for inflating balloons and airships, although its inflammability makes it dangerous for this purpose. Within the last few years, however, another gas, helium, has been used in America for filling airships. It has the advantage of being incombustible, and although denser than hydrogen, has almost as much lifting power.

Hydrogen gas is not poisonous, but if it were breathed it would prevent oxygen having access to the lungs, and so cause death by suffocation, as oxygen is necessary for the support of animal life.

Hydrogen burns readily and gives an extremely hot flame. In the oxy-hydrogen blowpipe, oxygen and hydrogen are burned together in a special jet, giving one of the hottest flames known. If this flame is directed on to a small cylinder of quicklime, the lime becomes incandescent and gives out an intense white light called limelight. The oxy-hydrogen flame is also used for melting and welding metals. The process of welding consists in joining two pieces of metal, for example, two tramway rails, by pressing their ends together and keeping the flame in contact with them until they melt into one another. When cold this gives a very strong joint.

Hydrogen can be burned like coal gas. A metal jet is prefer-

able, or a piece of the stem of a clay pipe, as a glass jet, unless the glass is very hard and infusible, closes up quickly owing to the heat of the flame. Before igniting a jet of hydrogen we must make certain (in the manner already explained), that the gas is not mixed with air, as this mixture is explosive. The most explosive mixture is made by mixing two parts by volume of hydrogen with one part of oxygen, or five parts of air.

Expt.—Fill a soda-water bottle with water and place it on the beehive in a pneumatic trough. Fill it two-thirds full with hydrogen and then add the remaining third of oxygen. Cork it under water, wrap it round with a duster and lay it on the bench. Light a taper, remove the cork, and holding the taper at arm's length, apply it to the mouth of the bottle.

Kipp's apparatus is convenient for a supply of hydrogen at any time. Granulated zinc is placed in the centre bulb and dilute hydrochloric or dilute sulphuric acid is poured into the opening at the top till the lower bulb is full and the acid covers the zinc. The tap is then closed, the pressure of the gas forces the acid out of the centre bulb, and as it is no longer in contact with the zinc, the action ceases. When a supply of hydrogen is desired the tap is opened, the pressure is thus released and the acid flows back into the centre globe, comes in contact with the zinc and produces hydrogen.

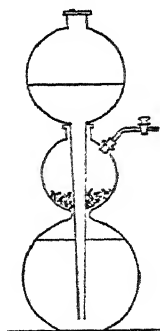
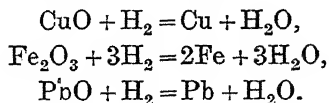


FIG. 43.

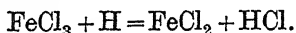
Hydrogen does not combine readily with most of the elements, but its affinity for oxygen is so great that it will remove oxygen from many of its compounds. This property is particularly useful in the extraction of metals from their oxides. We have already made use of it in measuring the equivalent of copper, and the same experiment may be repeated with the oxides of iron and lead. The equations are :



An action of this kind is termed **Reduction**, and hydrogen and other substances which act similarly are called **Reducing**

Agents. The opposite process is termed **Oxidation**, and oxygen and potassium chlorate are **Oxidizing Agents**. Generally speaking, oxidizing agents are those which can give up oxygen to other substances, reducing agents are those which can abstract oxygen from other substances. Oxidation means combination of oxygen with an element or compound, and reduction the removal of oxygen from a compound. We will go into this subject more fully at a later stage.

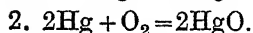
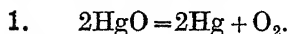
Nascent Hydrogen. When hydrogen is produced, by the action of zinc on sulphuric acid for example, it has at the moment of liberation a more powerful reducing action than ordinary gaseous hydrogen. If ordinary hydrogen is bubbled through a solution of yellow ferric chloride nothing happens, but if the hydrogen is generated in the solution by means of zinc and hydrochloric acid, reduction takes place and the yellow colour disappears.



It is generally supposed that the hydrogen at the moment of liberation is in the atomic state, as shown in the equation, and that it is more active then than it is after the atoms have united to form hydrogen molecules. It is consequently called **Nascent hydrogen**, which means hydrogen at the moment of birth. Oxygen and some other elements are also more active in the nascent state.

Reversible Reactions. Some physical changes are *reversible*. We can melt a metal by heating it and solidify it again by cooling. We can transform water into steam and condense the steam into water. These changes may be repeated an indefinite number of times.

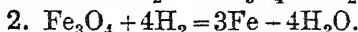
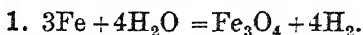
Similarly, many chemical changes are reversible. We have seen that Priestley prepared oxygen by heating red calx of mercury, and that Lavoisier heated mercury in air and obtained the red calx. The equations for these reactions are



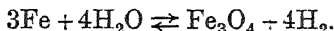
One reaction is obviously the reverse of the other, and the reaction between mercury and oxygen is consequently termed a *reversible* reaction.

When iron is heated in a current of steam it is oxidized to the magnetic oxide of iron, Fe_3O_4 , and hydrogen is set free.

But if the oxide is heated in a current of hydrogen it is reduced to metallic iron. The equations are :



This is also a reversible reaction. We may suppose that both reactions go on simultaneously. In reaction 1, as usually performed, there is a large excess of steam which carries away the hydrogen so fast that it has little reducing action on the oxide. In reaction 2, there is a large excess of hydrogen, so that the steam formed is carried away before it can oxidize the metallic iron. This is known as *mass action*. Reversible equations are generally written with two arrows pointing in opposite directions, thus :



The Commercial Preparation of Hydrogen

1. Hydrogen is made in large quantities by passing steam over heated iron.

2. A second method is the electrolysis of water, which gives a purer gas, and also gives oxygen.

3. When steam is blown through white hot coke 'water gas' is produced, a mixture of hydrogen and carbon monoxide. The separation of hydrogen from water gas will be discussed in the chapter on carbon monoxide.

4. Hydrogen is also obtained as a by-product in the Castner-Kellner process for making sodium hydroxide (p. 217).

The hydrogen prepared by these methods is compressed and stored into iron cylinders.

The Commercial Uses of Hydrogen

1. It is used for the inflation of balloons and airships.

2. Large quantities are employed in the important process known as the 'Hydrogenation of Oils.' By this process, vegetable oils such as cotton-seed oil, and animal oils like whale oil and fish oil, can be converted into fats. Many of these oils have a disagreeable taste or odour, which is completely removed in the process. The fats are used in making soap and candles, and for edible purposes in margarine. The oil is mixed with finely divided metallic nickel, which acts as a catalyst, heated

to 200° , and hydrogen is passed through the mixture. This has the effect of hardening the liquid oils into solid fats.

3. Hydrogen is also used in the preparation of ammonia from atmospheric nitrogen, a process to be explained later.

4. The oxy-hydrogen blowpipe used for welding requires hydrogen. A new development in this direction is the 'atomic hydrogen welding torch,' which gives a heat far greater than any gas flame. When an electric arc is made to burn between tungsten electrodes in an atmosphere of hydrogen, some of the hydrogen molecules (H_2) in contact with the arc are split up into atoms of hydrogen (H). Beyond the arc these atoms immediately re-combine with evolution of much heat. The atomic hydrogen torch will melt tungsten, which has the highest melting point of all the metals (3500°), and can be used for welding metals which can only be melted with difficulty by other methods.

Additional Experiments

EXPT.—Place some powdered calcium in a test tube. Immerse it in water and collect the hydrogen in a jar.

EXPT.—To blow soap bubbles with hydrogen, pass the hydrogen from the Kipp or generating flask through caustic soda solution to remove the acid spray which destroys the soap film. Attach a clay pipe to the generator by a piece of rubber tube.

EXPT.—To collect hydrogen displaced from water by sodium or potassium. A cage may be made of copper wire gauze. The gauze

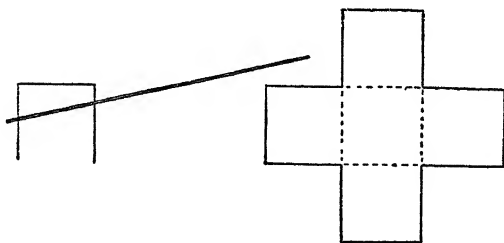


FIG. 44.

is cut to shape and bent along the dotted lines to form a lidless box, and a piece of stout copper wire is attached to form a handle.

EXPT.—The following is a safe method of shewing the action of sodium on water. Take a glass tube $\frac{1}{2}$ -inch internal diameter and

3 inches long. Clamp it vertically above a trough, immersing it in the water to a depth of 1 inch. Take care that the inside of the tube above the water level is perfectly dry. Drop into it a piece of sodium. The hydrogen may be ignited at the top of the tube.

EXPT.—Show that hydrogen is obtained by the action of caustic soda on aluminium and zinc.

EXPT.—Reduce ferric oxide and litharge in hydrogen.

EXPT.—To show the greater activity of *nascent* hydrogen. Take very dilute solutions of potassium permanganate and potassium dichromate. Acidify them with sulphuric acid. Through one pair pass hydrogen gas. To a second pair add zinc.

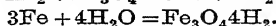
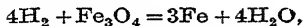
QUESTIONS

1. Explain clearly how oxygen can be removed from water by means of (a) sodium, (b) magnesium, (c) iron. Describe fully how you would carry out the experiments, stating in each case what substances would be produced and how you would obtain specimens of them. (London Matric.)

2. Describe, with a sketch of the apparatus, how you would prepare dry hydrogen. What do you understand by the term nascent hydrogen? Explain carefully how you would make use of hydrogen to reduce (a) copper oxide to copper, (b) a solution of ferric chloride to ferrous chloride. (London Matric.)

3. Write a clear explanatory note on the use of helium in airships. (Scot. Leaving Cert.)

4. Define reversible reaction.



Describe briefly how you would perform the experiments represented by these equations, and account for the apparent contradiction. (Scot. Leaving Cert.)

5. Describe fully the method you would adopt in order to determine the volume of hydrogen liberated when 1 gram of zinc is dissolved in dilute acid. Supposing in such an experiment 100 c.c. of hydrogen at 26° C. and 740 mm. were obtained, what weight of zinc must have been used? (London Matric.)

CHAPTER XIV

WATER

PURE water is a clear, colourless, odourless and tasteless liquid. When heated to 100°C . it boils and is changed into steam. Steam is a colourless vapour.

EXPT.—Boil some water in a flask. Observe that inside the flask the steam is invisible, but when it meets the air it becomes visible as mist. The colder air condenses the steam to a cloud of minute droplets of liquid water.

When water is heated the activity of the molecules is increased, and they escape from the surface in greater numbers as the temperature rises. Finally they cannot escape sufficiently quickly from the surface, and bubbles of steam form in the liquid which increase in size as they rise, and pass into the air. This is known as **Boiling**. At a pressure of 760 mm. water boils at 100°C . When the pressure is decreased there is less resistance to the molecules flying off through the surface, so that the water boils at a lower temperature. At the top of a high mountain, boiling water may not be hot enough for cooking purposes.

Water freezes at 0°C . into solid ice. Like most liquids, its volume expands when heated and contracts when cooled. This contraction continues till water is cooled down to 4°C ., when it begins to expand, and continues to do so until it is changed into ice. Ice is therefore lighter than water. When the water of a lake becomes cooled at the surface, it contracts and the heavier water sinks, while the lighter rises to take its place. This circulation proceeds until all the water has been cooled to 4°C . With further cooling, the surface layer expands and ceases to sink, and finally, if the temperature is low enough, it freezes to a sheet of ice, which floats on the water. If water

continued to contract down to the freezing point, lakes and rivers might, in a severe winter, freeze from the bottom upwards into a solid mass, upon which the rays of the summer sun would have little effect. Our climate, instead of being temperate, would become Arctic. This expansion of water during freezing is a cause of the weathering or disintegration of rocks and building stone. The water which finds its way into the crevices expands when it freezes, and bursts the rocks asunder. Water pipes frequently burst from this cause, but the resulting leak is not, of course, discovered till a thaw sets in and melts the ice.

Natural waters—rain water, spring water, river water, sea water—all contain solid and gaseous impurities. Rain water contains the least solid impurity. In its descent, it collects dust, and dissolves from the atmosphere, oxygen, nitrogen, and other gases. When it reaches the ground it begins to dissolve various substances from the soil and the rocks, so that spring or well water which has passed through a considerable thickness of soil contains a greater amount of solids. River water also carries solid matter in solution and suspension, derived from the rocks, soils, and vegetation through which it has flowed. These solids are finally carried to the sea. Sea water contains about $3\frac{1}{2}\%$ of dissolved solids, of which $2\frac{1}{2}\%$ is common salt.

EXPT.—To show that gases are dissolved in water. Boil some tap water in a flask and observe that bubbles of gas rise to the surface before the water actually boils. Gases are usually more soluble in cold than in hot water, and are therefore expelled on heating.

EXPT.—Attach a leading tube to a 1000 c.c. flask with a one hole rubber stopper. Fill the flask and leading tube full with water, and press the stopper in firmly. The tube should be flush with the bottom of the stopper, and there must be no air in the flask or tube. Support the flask on a wire gauze and connect the leading tube with a small graduated cylinder filled with water in a pneumatic trough. Boil till gas ceases to collect in the jar, the steam is condensed by the cold water. Calculate

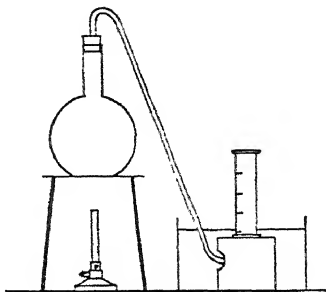


FIG. 45

the quantity of gas contained in one litre of water, having measured the exact volume of the flask.

Solids in Water. The total solids can be estimated by evaporating a definite weight of water to dryness, in a weighed porcelain basin. The weight of the dry residue may be calculated as a percentage of the weight of the water.

Distillation. Water can be purified by distillation.

EXPT.—Fit up a distillation apparatus as shewn in the diagram. *A* is the boiling flask, *B* is the condenser, *C* is the receiver. The

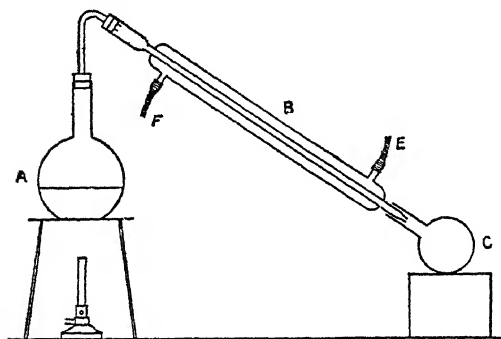


FIG 46.

condenser is connected by the rubber tubing *E* to a water tap, and by tubing *F* to a sink. During the distillation a constant stream of cold water flows through the jacket of the condenser and condenses the steam. The water in flask *A* may be coloured by adding a little potassium permanganate, which gives it a purple tint.

Bring to the boil and observe that the water which collects in the receiver is colourless. When the receiver is half full, remove it and evaporate the distillate to dryness. Compare the residue with that obtained from an equal quantity of tap water.

Composition of Water. We know that certain metals can set free hydrogen from water, and that magnesium heated in steam is changed into magnesium oxide, exactly the same substance as is formed when the metal is burned in oxygen. We therefore infer that water contains hydrogen and oxygen. It can be shewn that 2 volumes of hydrogen combine with 1 volume of oxygen to form water, and its formula is H_2O . It can be decomposed into its constituents by the electric current by the process of **Electrolysis**. The following experiment may be performed by the teacher.

EXPT.—The apparatus, known as a **Voltameter**, consists of a glass bulb with three limbs. The centre limb ends in a bulb

reservoir, and the side limbs are fitted with stop-cocks. Each of them also contains a piece of platinum foil connected to a wire which passes through the glass and ends outside in a loop. To these loops are attached wires leading to a battery of accumulators, or D.C. mains current may be used with lamp resistances in circuit. The tubes are filled with acidulated water up to the stop-cocks, which are then closed. Pure water is a very bad conductor of electricity, so a little sulphuric acid must be added, which acts as a carrier of the current. On connecting up with the battery, the current passes through the liquid from one platinum plate to the other. Bubbles of gas appear and collect in the tubes. When the experiment has proceeded for a minute or two it will be obvious that the volume of one gas, hydrogen, is twice the volume of the other, oxygen. The hydrogen may be tested with a flame, and the oxygen with a glowing wood splint.

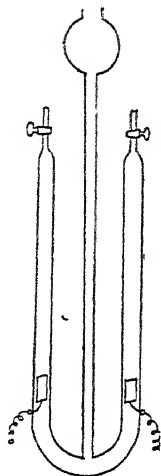


FIG 47—Volta-meter

The current is considered to flow from positive to negative through the water. The hydrogen goes with the current and appears at the negative electrode or Cathode, the oxygen travels in the opposite direction and comes off at the positive electrode or Anode. This experiment does not really prove that water is composed of hydrogen and oxygen. These may come from the sulphuric acid, which also contains hydrogen and oxygen. It can be shown, however, that the quantity of the sulphuric acid does not decrease during the process, and there are other considerations which lead us to the conclusion that the water only is decomposed.

Water is formed when hydrogen is burned in air.

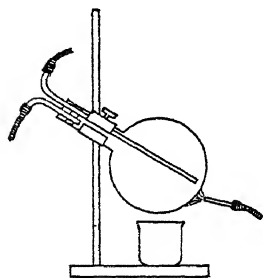


FIG 48

EXPT.—Fix a round-bottom 500 c.c. flask in a clamp. Fit it with a two hole rubber stopper carrying two pieces of bent glass tubing, one reaching to the bottom of the flask and connected by a length of rubber tubing to the water tap, the other connected similarly with the sink. Open the water tap and fill the flask, the circulation of cold water prevents the glass from melting. Arrange a Kipp or

other hydrogen apparatus and dry the gas by passing it through strong sulphuric acid. Burn it from a metal jet, holding the flame against the flask. As usual, before lighting the jet, make sure that all air has been driven out of the apparatus. Drops of liquid soon collect and fall into a beaker placed to receive them. Satisfy yourself that the liquid in the beaker has the properties of pure water, taste, smell, no action on litmus paper, turns white anhydrous copper sulphate blue, leaves no residue on evaporation. If sufficient is collected, the density and boiling point may be measured.

The composition of water can be demonstrated by the method of **Synthesis**. This experiment may be performed by the teacher.

Expt.—The simplest form of the Eudiometer, in which the synthesis is carried out, is a thick-walled glass tube, graduated, and closed at one end. Near the closed end two platinum wires are sealed into the glass and nearly meet inside the tube. On connecting these with an induction coil, a spark can be obtained. The tube is filled with mercury, inverted over a mercury trough and clamped in position. Hydrogen which has been thoroughly dried is passed into the tube. The mercury levels in the trough and tube are then accurately read. The difference between the two levels is subtracted from the barometric pressure, and the volume of the gas corrected to N.T.P. Oxygen is added, in volume about $\frac{1}{4}$ that of the hydrogen, and the total volume similarly corrected to N.T.P. The eudiometer is then closed by pressing firmly upon a piece of rubber under the mercury and clamped, and the mixture is fired by the electric spark. After it is cool the tube is raised, the mercury levels are read as before and the volume of the remaining hydrogen is corrected to N.T.P. Calculation will show that combination has taken place in the proportion of 2 volumes of hydrogen to 1 volume of oxygen.

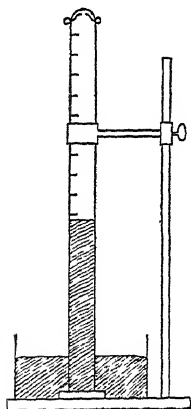


FIG. 49 — Eudiometer

This is, in principle, the same method as that used by Henry Cavendish in his classical research which resulted in the discovery of the composition of water. Priestley had noticed (1781) that when a mixture of common air and inflammable air (hydrogen) was fired in a dry vessel, the inside of the vessel became dewy. Cavendish (1784) repeated this experiment and

found that when inflammable air is exploded with about $2\frac{1}{2}$ times its volume of common air, the inflammable air and about $\frac{1}{5}$ of the common air are turned into pure water. Just 10 years before, Priestley had discovered dephlogisticated air or oxygen, and Cavendish, knowing its properties as a supporter of combustion, substituted it for common air in his experiments. He used a glass globe furnished with a stop-cock and an apparatus for firing gas by electricity. The globe was exhausted by an air-pump and filled from a reservoir with a mixture of 2 parts of inflammable air to 1 part of dephlogisticated air. 'The air was then fired by electricity, by which means almost all of it lost its elasticity.' The globe was again connected with the reservoir and filled with the mixed gases, and the process repeated until the supply was used up, 'without any fresh exhaustion of the globe.' By this means Cavendish obtained 30 grains of water, and finally disproved the old theory that water was an element by shewing that it could be produced by the union of the two gases which we now call hydrogen and oxygen.

The molecular weight of water is 18, of which 16 parts are oxygen and 2 parts hydrogen. These proportions by weight can be verified by carrying out quantitatively an experiment already performed in Chap. VIII, the reduction of black copper oxide by hydrogen.

EXPT.—Fit up the apparatus as in the former experiment, and attach a calcium chloride U-tube to the tube containing the oxide. Calcium chloride is a deliquescent substance which readily absorbs moisture, and is used for drying gases—in this case for collecting the water produced in the reaction. Weigh the tube and contents before and after reduction, the difference gives the weight of oxygen in the water which is formed. Weigh the drying tube before and after the experiment, the increase of weight represents the weight of water. From these data calculate the weight of hydrogen which combines with 16 grams of oxygen.

J. Dumas (1843) investigated the composition of water by weight very carefully. He passed hydrogen, which had been thoroughly purified, over heated copper oxide, and absorbed the water produced in tubes containing solid potassium hydroxide and phosphorus pentoxide. The average of his results shewed that 16 parts by weight of oxygen combine with 2.004 parts of hydrogen. An American chemist, Morley, fifty years later performed some very accurate determinations of

the composition of water. He burned hydrogen in oxygen and found the oxygen:hydrogen ratio to be 16:2.015. The weight of 2 atoms of hydrogen is therefore 2.015, and if 16 be taken as the atomic weight of oxygen, the atomic weight of hydrogen is 1.008.

QUESTIONS

1. The following is the percentage composition of water; oxygen 88.82, hydrogen 11.18. How has this been arrived at? What other facts are expressed by the formula H_2O ?
(Oxford and Camb. School Cert.)

2. Give some account of the researches on the composition of water by (1) Cavendish, and (2) Dumas.

3. How would you ascertain whether a sample of water had dissolved any air and, if so, how would you measure approximately the volume of it contained in one litre of the water? Given a 500 c.c. stoppered flask containing 'recovered air,' describe in detail how you would find out whether it differed in composition from ordinary air.
(London Matric.)

4. A eudiometer contains a mixture of nitrogen and hydrogen measuring 25 c.c.; 10 c.c. of oxygen are added and the mixture is exploded. After the remaining gas has cooled it measures 20 c.c. Calculate the volume of hydrogen in the original mixture.

5. State the chemical differences between rain water, river water, spring water, and sea water, and describe experiments which will illustrate these differences.
(London Matric.)

6. Describe carefully and with full experimental detail, an experiment by which you could determine the amount of dissolved salts present in a given volume of sea water. How could you show that the principal substance dissolved in sea water is sodium chloride?
(London Matric.)

CHAPTER XV

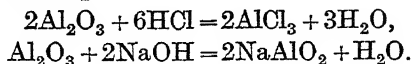
OXIDES. OXIDATION AND REDUCTION. OZONE. HYDROGEN PEROXIDE

Basic and Acidic Oxides. We have already studied two classes of oxides, basic and acidic. Metals form basic oxides, non-metals form acidic oxides. As the valency of an element increases, its power of combination with oxygen increases, it has more hooks to grasp oxygen atoms. Thus many of the metals form more than one oxide, manganese for example forms 6. The lower oxides—those with the smaller proportion of oxygen—are generally basic, but many of the higher oxides are acidic. Chromium forms an oxide CrO_3 , from which is derived chromic acid. Manganese forms an oxide Mn_2O_7 , which is the anhydride of permanganic acid.

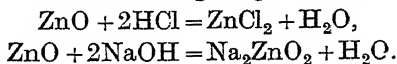
Neutral Oxides. The oxides derived from the non-metals are not all acidic. For example, solutions of carbon monoxide, CO, and nitrous oxide, N_2O , do not react with litmus. Such oxides may be called 'neutral' oxides.

Amphoteric Oxides. A base is sometimes defined as a substance which, when acted upon by an acid, gives a salt and water. A few bases also behave like acids, when acted on by a base they give a salt and water.

Aluminium oxide, Al_2O_3 , prepared by gently heating the hydroxide, $\text{Al}(\text{OH})_3$, dissolves in hydrochloric acid giving aluminium chloride, AlCl_3 , and in caustic soda giving sodium aluminate, NaAlO_2 .



Aluminium hydroxide reacts in a similar way. Zinc oxide and zinc hydroxide also dissolve in hydrochloric acid giving zinc chloride, and in caustic soda giving sodium zincate.



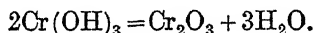
Thus aluminium and zinc oxides act towards acids like bases and towards bases like acids. Such oxides are usually called **Amphoteric Oxides**, from a Greek word meaning 'both'. Observe that when a base acts on zinc or aluminium oxide the metal is in the acid or negative radical of the salt formed, AlO_2^- and ZnO_2^{--} . See p. 126.

Peroxides. There are also the 'peroxides.' They generally have 2 atoms of oxygen in the molecule, and contain more oxygen than the basic oxide. Examples of the metallic peroxides are, lead peroxide, PbO_2 , and sodium peroxide, Na_2O_2 . Some non-metallic peroxides are, hydrogen peroxide, H_2O_2 , and chlorine peroxide, ClO_2 . The peroxides are usually good oxidizing agents and give off oxygen when heated.

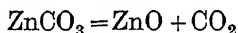
Preparation of Oxides

1. Non-metallic acidic oxides can generally be made by heating the element in oxygen; we have already made CO_2 , SO_2 , and P_2O_5 in this way. They are soluble in water and the solution has an acid reaction.

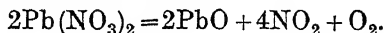
2. Basic oxides can also be made by heating the metal in oxygen. In addition, certain metallic compounds such as hydroxides, carbonates, and nitrates, decompose on heating, leaving the basic oxide. Thus, chromium hydroxide gives chromic oxide,



Zinc carbonate gives zinc oxide,

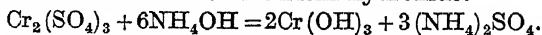


Lead nitrate gives lead monoxide,

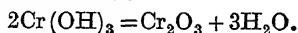


3. For the preparation of the other classes of oxides no general methods can be given.

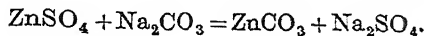
EXPT.—To prepare chromic oxide. Take some chromium sulphate in a beaker, dissolve in water, heat to boiling and add dilute ammonium hydroxide drop by drop till no further precipitate appears. Filter off the chromium hydroxide.



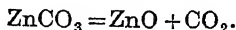
Wash the precipitate with hot water, scrape it off the filter paper and transfer to a crucible. Heat until the hydroxide is decomposed into green chromic oxide.



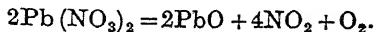
EXPT.—To prepare zinc oxide from zinc carbonate, ZnCO_3 . Take some zinc sulphate solution in a beaker and add sodium carbonate solution. A white precipitate of zinc carbonate is obtained.



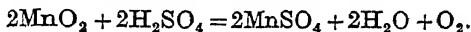
Wash the precipitate with warm water and transfer to a crucible. Take a small quantity in a test tube and add dilute hydrochloric acid, note the effervescence due to the presence of carbonate. Cover the crucible with a lid and heat till a small portion gives no effervescence with acid. The white substance left is zinc oxide, ZnO .



EXPT.—Prepare lead monoxide by heating lead nitrate. Heat a little solid lead nitrate in a crucible till yellow lead monoxide is left.



EXPT.—Test for peroxides. Heat some manganese dioxide in a test tube with a little concentrated sulphuric acid, and test for oxygen with a glowing wood splinter. Peroxides give off oxygen when heated with concentrated sulphuric acid.



Caution. *Be careful when using strong sulphuric acid that it does not come in contact with the skin or clothes. Never pour hot sulphuric acid into the sink, as it may spirt in your face, allow it to cool first. When mixing sulphuric acid with water always pour the acid into the water.*

EXPT.—Heat a little manganese dioxide with concentrated hydrochloric acid in a test tube. Note that a greenish gas is given off which has a pungent smell. This is chlorine. Peroxides oxidize hydrochloric acid, setting free chlorine.

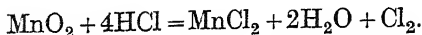


Oxidation

1. Oxygen gas is the primary **Oxidizing Agent**, and the simplest example of oxidation is the burning of a metal or non-metal in oxygen, the process known as combustion. Some metals, such as gold and silver, do not unite with oxygen directly, and are called the 'noble' metals, probably because the nobles in days of old did not associate with common people.

2. Substances containing oxygen may give up their oxygen to oxidize other substances. Manganese dioxide oxidizes

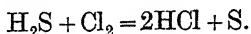
hydrochloric acid when a mixture of these substances is heated,



In this reaction the manganese dioxide gives up its oxygen to oxidize the hydrogen of the hydrochloric acid to water.

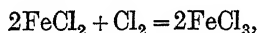
3. Removal of hydrogen may also be regarded as an oxidizing action. In the last reaction, chlorine gas, Cl_2 , is a product of oxidation but contains no oxygen; hydrogen has been removed from the hydrochloric acid, setting free chlorine.

When hydrogen sulphide and chlorine gases are mixed, they react together, setting free sulphur,



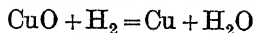
Chlorine here acts just like oxygen in removing hydrogen, and is in consequence regarded as an oxidizing agent, although no oxygen appears in the reaction.

4. The term oxidation may therefore be extended to include reactions in which there is no oxygen involved. When ferrous chloride is changed to ferric chloride it is said to be oxidized,



and we may take it as a general rule that 'a chemical change which increases the proportion of the negative radical or reduces the proportion of the positive radical in a molecule is an oxidation.' If the proportion of the negative radical is increased, it follows that the 'active' valency of the positive radical must be correspondingly increased. In the oxidation of ferrous chloride the valency of the iron atom has increased from 2 in the ferrous state to 3 in the ferric state. Hence a reaction which causes an increase in the active valency of the positive radical is an oxidizing action. For explanation of the term 'radical,' see next chapter

Reduction. We should realise that oxidation is always accompanied by reduction, that the substance which is oxidized acts as a Reducing Agent. In the reaction



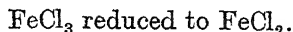
the copper oxide is the oxidizing agent and the hydrogen the reducing agent.

1. Hydrogen is the primary reducing agent, and the simplest example of reduction is the one just given. Many of the

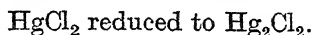
metallic oxides can be reduced to the metallic state by heating in a current of hydrogen.

2. Reduction is just the converse of oxidation, it may be either a giving of hydrogen or a taking away of oxygen.

3. In reactions in which no oxygen takes part, reduction means reducing the proportion of the negative radical or increasing the proportion of the positive radical. Ferric chloride is reduced to ferrous chloride,



Mercuric chloride is reduced to mercurous chloride,



4. In reduction, the active valency of the positive radical is reduced, Fe^{+++} becomes Fe^{++} , Hg^{++} becomes Hg^+ . See next chapter.

Ozone. O_3 .

Occurrence. The health-giving properties of seaside air are popularly supposed to be due in part to the presence of ozone. This is doubtful, as the usual tests for ozone are really only tests for oxidizing substances. There appears however to be no doubt that it is formed in the atmosphere during thunderstorms.

Ozone is a gas with a characteristic smell which is difficult to describe, but may be observed in a physical laboratory when an electrical machine is working. It was this that attracted the attention of Schonbein (1840). He noticed that the same odour was produced during the slow oxidation of phosphorus and the electrolysis of water. Schönbein considered that the odour was due to the presence of a definite chemical substance, to which he gave the name Ozone, from a Greek word meaning 'smell,' but did not discover its composition.

Preparation of Ozone

1. The most convenient method of preparation is to use an ozonizer as illustrated. A slow current of oxygen is passed through the space between the inner and outer tubes. The wires *A* and *B* are connected with a sparking coil and battery, and dip into dilute sulphuric acid in the tube and beaker. A silent electrical discharge is produced between

the wires which converts part of the oxygen into ozone, the yield is seldom greater than 6-7%.

2. Ozone is formed during the slow oxidation of phosphorus.

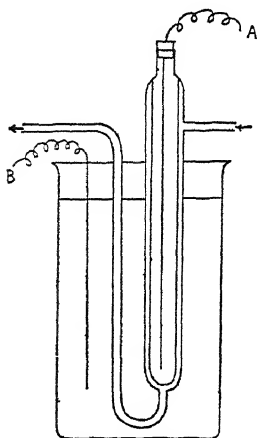
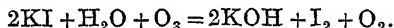


FIG 50 —Ozonizer.

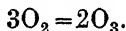
EXPT.—Place a clean stick of phosphorus in a stoppered bottle with a little water—not sufficient to cover it. After some time remove the stopper and observe the peculiar smell. Introduce into the bottle a piece of starch iodide paper, made by dipping filter paper in a mixture of potassium iodide and starch solutions. Ozone turns this paper blue by oxidizing the potassium iodide, setting free iodine, thus,



The iodine then unites with the starch, giving a deep blue colour. This is not a conclusive test for ozone, as chlorine and some other oxidizing agents give the same reaction.

Composition of Ozone. Ozone is a form of oxygen. We shall see that many of the elements can exist in more than one variety. Carbon, sulphur, and phosphorus have each several different forms. Such differences may be due to a change in crystalline state, or to a change of number or a new arrangement of atoms in the molecule. This phenomenon is called **Allotropy**, and the various forms which an *element* can assume are called **Allotropic modifications**.

Ozone contains 3 atoms of oxygen in the molecule, and its formula is O_3 . Soret (1866), shewed that 3 volumes of oxygen when changed into ozone occupy 2 volumes, thus,



His method depends on two properties of ozone.

1. If a mixture of oxygen and ozone is shaken up with turpentine, the ozone is dissolved and removed from the mixture.

2. If ozone is heated it is decomposed into oxygen.

A measured volume of oxygen containing ozone is shaken with turpentine and re-measured. Suppose the contraction of

volume is 4 c.c. This represents the volume of ozone. An equal volume of the same mixture is then heated, and the expansion after cooling is found to be 2 c.c. Thus 4 c.c. of ozone on heating give $4+2=6$ c.c. of oxygen, and by Avogadro's hypothesis, 4 molecules of ozone give 6 molecules of oxygen. But 6 molecules of oxygen contain 12 atoms, therefore 4 molecules of ozone contain 12 atoms of oxygen and 1 molecule contains 3 atoms. Hence its formula is O_3 .

The density and molecular weight of ozone have been determined by comparing its rate of diffusion with that of other gases. According to Graham's law of diffusion, the ratio of the rates of diffusion of gases are inversely proportional to the square roots of their densities.

Properties of Ozone

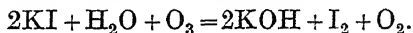
1. It is a powerful oxidizing agent as the molecule easily gives up an atom of oxygen. It readily attacks most metals forming oxides. If a globule of mercury is shaken in a flask containing some ozone it loses its lustre and forms a film on the surface of the glass. It oxidizes potassium iodide, setting free iodine as already explained.

2. It bleaches litmus and indigo solution.

3. It attacks cork and indiarubber.

4. It is decomposed into oxygen on heating to $250^\circ C$.

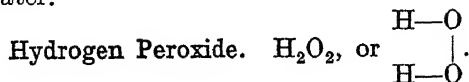
5. It may be distinguished from other oxidizing agents (except hydrogen peroxide) by testing with pink litmus paper dipped in potassium iodide solution.



The potassium hydroxide produced turns the litmus paper blue.

Uses of Ozone

It has been used for purifying air, but there is proof that the small quantities employed have no destructive effect on germs. It has also been used with success for sterilizing water.

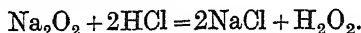


Occurrence. This substance is said to be found in small

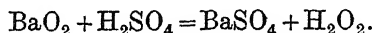
quantities in snow and rain, but its presence, like that of ozone, is doubtful, and for the same reason.

Preparation. Hydrogen peroxide is prepared by the action of cold dilute acids on metallic peroxides.

1. Add dilute hydrochloric acid to a solution of sodium peroxide in ice-cold water, a solution of sodium chloride and hydrogen peroxide is obtained.

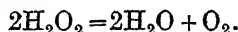


2. Barium peroxide suspended in water is added to a mixture of 1 part of sulphuric acid with 1 part of water, cooled in a freezing mixture, until the liquid is almost neutral to litmus.



The insoluble barium sulphate is filtered off and a solution of hydrogen peroxide is obtained.

Properties. Pure hydrogen peroxide is a colourless syrupy liquid, Sp. Gr. 1.5. Its formula is H_2O_2 . It has no smell. When heated, hydrogen peroxide and its solutions decompose, giving water and oxygen.

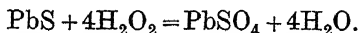


Hydrogen peroxide is consequently a good oxidizing agent.

1. Like ozone, it oxidizes potassium iodide, liberating iodine.

EXPT.—Add a little hydrogen peroxide to potassium iodide solution in a test tube, the solution turns brown from the liberated iodine. If a few drops of starch solution are then added, a blue colour is obtained.

2. Hydrogen peroxide oxidizes black lead sulphide to white lead sulphate.



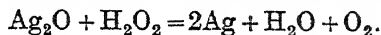
EXPT.—Wet a piece of filter paper with lead acetate solution and blacken it by holding in a stream of hydrogen sulphide. It is bleached by dipping in hydrogen peroxide.

3. It reacts with bases, giving peroxides.

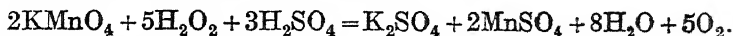
EXPT.—Ten c.c. of 20% sodium hydroxide is placed in a small flask and 4 c.c. of 20 volume hydrogen peroxide is added and shaken. Add 20 c.c. of absolute alcohol, the mass solidifies, giving crystals of sodium peroxide, $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$.

EXPT.—Add hydrogen peroxide to barium hydroxide solution; barium peroxide, $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$ is precipitated.

Hydrogen peroxide appears to act as a reducing agent also. With oxide of silver, Ag_2O , it gives metallic silver and oxygen.



Potassium permanganate solution acidified with sulphuric acid is decolorised by hydrogen peroxide.



These are not really reducing actions. The two substances contribute each an equal number of oxygen atoms, which mutually oxidize each other, forming oxygen molecules. The basis of the reaction is the readiness of both substances to give up oxygen.

Uses of Hydrogen Peroxide. It is used in cleaning old paintings. White lead, basic lead carbonate, is used as an artist's colour. This blackens with age, being converted into black lead sulphide by the action of the hydrogen sulphide, which is present particularly in the air of towns. As we have seen, this is bleached to white lead sulphate by the application of hydrogen peroxide, and the colour is thus restored to its original brightness. People who wish to change the colour of their hair frequently bleach it to a golden yellow by means of hydrogen peroxide. It also bleaches ivory, feathers, silk and teeth. Hydrogen peroxide has antiseptic properties and is used in the treatment of wounds and as a mouth wash and dentifrice.

EXPT.—Test for H_2O_2 . Acidify some peroxide solution with dilute sulphuric acid, and add a little potassium dichromate solution and a few drops of ether. Shake up, the ether layer shows a blue colour.

Hydrogen peroxide is usually sold as 10 volume and 20 volume solution. This means that 1 c.c. gives 10 c.c. of oxygen in the first case, and 20 c.c. in the second. This is equivalent to a strength of 3% and 6% respectively. The relationship between volume and percentage strength may be calculated in this way.

The molecular weight of H_2O_2 is $2 + 32 = 34$.

Two molecules of H_2O_2 give one molecule of oxygen.

One gram molecule of oxygen occupies 22.4 litres at N.T.P.

∴ 68 grams of H_2O_2 give 22400 c.c. of oxygen,
and 1 gram of H_2O_2 gives $\frac{22400}{68} = 329$ c.c. of oxygen.

The dilute solution of H_2O_2 may be taken as having the same specific gravity as water, 1 c.c. = 1 gram ;

∴ 1 c.c. of H_2O_2 gives 329 c.c. of oxygen,
or 1 c.c. of 100% H_2O_2 gives 329 c.c. of oxygen,
and 1 c.c. of 1% H_2O_2 gives $\frac{329}{100} = 3.3$ c.c. of oxygen,
and 1 c.c. of 3% H_2O_2 gives $3.3 \times 3 = 10$ c.c. of oxygen ;
∴ 10 volume H_2O_2 is 3% strength.

The metallic peroxides are often divided into 2 classes, the true peroxides and the dioxides. The former give hydrogen peroxide when acted on by dilute acids, while the latter do not

Thus barium peroxide, BaO_2 or $\text{Ba} \begin{array}{c} \diagup \text{O} \\ | \\ \diagdown \text{O} \end{array}$, and sodium peroxide, Na_2O_2 , or $\begin{array}{c} \text{Na}-\text{O} \\ | \\ \text{Na}-\text{O} \end{array}$, are true peroxides resembling hydrogen peroxide in structure, while lead peroxide, PbO_2 or $\text{Pb} \begin{array}{c} \diagup \text{O} \\ | \\ \diagdown \text{O} \end{array}$, and manganese dioxide, MnO_2 or $\text{Mn} \begin{array}{c} \diagup \text{O} \\ | \\ \diagdown \text{O} \end{array}$, which do not give hydrogen peroxide with dilute acids, are classed as dioxides.

Additional Experiments

EXPT.—Put some barium peroxide in a test tube and add a drop of concentrated sulphuric acid. Observe the smell of ozone.

EXPT.—Attach a piece of rubber tubing to the outlet tube of the ozonizer, and note that the rubber perishes at the junction with the glass.

EXPT.—Pass the gas from the ozonizer through water coloured with indigo.

EXPT.—Arrange a small flask with dropping funnel and leading tube. Place in it some hydrogen peroxide and drop in acidified potassium permanganate. The oxygen may be collected and tested.

EXPT.—Add sodium hydroxide drop by drop to a solution of silver nitrate in a test tube till a precipitate of oxide of silver comes down. Then add a little hydrogen peroxide and shake. The oxide is reduced to metallic silver with evolution of oxygen.

QUESTIONS

1. Give examples shewing that some oxides may have both acid and basic properties. What name is applied to such oxides ?

2. Explain the terms 'oxidizing agent' and 'reducing agent.' Select from the following substances two examples of each and write an account of the experiments you would perform with them to illustrate your answer : hydrogen, carbon monoxide, chlorine, sulphur dioxide, nitric acid, potassium permanganate.

(Scot. Leaving Cert.)

3. Why do we call hydrogen a reducing agent ? Give an example of its action as such. Name two other gaseous reducing agents and one solid reducing agent and give examples of their reducing action.

(Scot. Univ. Entrance.)

4. In what category—viz. oxidizing or reducing agent—should each of the following gases be placed : hydrogen, nitrogen, ammonia, sulphur dioxide, chlorine ?

(Scot. Univ. Entrance.)

5. Explain how the term oxidation may be applied to a chemical reaction in which there is no oxygen involved.

6. How is ozone formed ? What are its properties ? On what evidence is O_3 taken as the formula of ozone ?

(Scot. Univ. Entrance.)

7. Compare the properties of oxygen and ozone. In what manner has the relationship between the two substances been established ?

(Scot. Univ. Entrance.)

8. What are the chief characteristics of hydrogen peroxide ? Give examples of its use as an oxidizing agent.

(Oxford and Camb. School Cert.)

9. What is the action of hydrogen peroxide on (a) potassium iodide solution, (b) potassium permanganate solution, (c) lead sulphide ?

CHAPTER XVI

METALS AND NON-METALS. ACIDS. ALKALIES. BASES. SALTS

THE elements are frequently divided into two classes, Metals and Non-metals. This is a convenient but not an exact classification, for there are a few elements which cannot be placed definitely in either class as they partake of the properties of both. The general characteristics of these two classes may be tabulated as follows :

Metals

Are solids, one or two, *e.g.* mercury, are liquids.

Have a metallic lustre.

Have high densities, except lithium, sodium, potassium, magnesium and aluminium.

Are good conductors of heat.

Are good conductors of electricity.

Are malleable and ductile, that is, they can be shaped with a hammer or drawn into wire. Bismuth and antimony are brittle.

Form basic oxides, a few form acidic oxides.

Form chlorides not decomposed by water. There are a few exceptions.

Form the positive radical in salts.

Non-metals

Are gases or solids.

Have no lustre, except iodine and graphite.

Have low densities.

Are bad conductors of heat.

Are bad conductors of electricity, except graphite.

Are neither malleable nor ductile.

Form acidic oxides.

Form chlorides decomposed by water.

Form the negative radical in salts.

To decide in which of these classes an element should be placed, we must consider all its properties. The statements in the table are obviously only true in general, as there are exceptions to practically all of them.

Acids. The first acid known to man was vinegar (acetic acid), which is formed when wine turns sour. Hydrochloric, sulphuric, and nitric acids were also known to the alchemists, who were acquainted with their corrosive and solvent properties. Lavoisier observed that when sulphur and phosphorus are burnt in oxygen the oxide produced unites with water to form an acid solution. He therefore concluded that all acids contained oxygen, and the name oxygen or 'acid former' is a reminder of this theory. By the year 1813, however, Humphry Davy had shewn that hydrochloric acid is a compound of hydrogen and chlorine and that hydriodic acid is a compound of hydrogen and iodine, neither of them containing oxygen. These discoveries led to the abandonment of the Lavoisier oxygen theory.

The acids most frequently used in the laboratory are hydrochloric acid, HCl , nitric acid, HNO_3 , and sulphuric acid, H_2SO_4 . They are kept in two strengths, concentrated or strong, and dilute. Care must be taken in using concentrated acids as they are extremely corrosive or burning.

Properties of Acids.

1. All acids have a sour taste.
2. All acids give a red colour with litmus.
3. Acids corrode and dissolve metals. One acid does not dissolve all metals, neither does one metal, generally speaking, dissolve in every acid

Expt.—Take a small piece of copper foil in a test tube and add dilute nitric acid. The metal dissolves, with evolution of brown fumes, and gives a blue solution.

Expt.—Test the action of dilute hydrochloric acid on another piece of copper. In this case there is no action.

Expt.—In the same way test a little granulated zinc with hydrochloric acid and nitric acid. In hydrochloric acid the zinc dissolves with evolution of hydrogen, but nitric acid has no action.

If the solvent action of an acid upon a metal is slow in the cold, it can frequently be accelerated by warming. Test this in above experiments.

4. Acids dissolve marble, limestone, and other members of the class of substances known as Carbonates. Carbon dioxide gas is evolved with effervescence.

EXPT.—Pour a little lime water into a test tube. Replace the tube in the test tube stand. Take another tube, drop into it two or three marble chips and add dilute hydrochloric acid. After the effervescence has continued for a minute or so, the tube will be filled with carbon dioxide gas. Pour the gas slowly into the lime-water tube, taking care that no acid goes with it (carbon dioxide is heavy and can be poured like water). Stop the tube with the thumb and shake up, the lime water turns milky. This is the usual test for a carbonate.

EXPT.—Repeat the experiment, using carbonate of soda instead of marble chips.

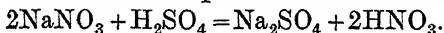
5. Acids are good conductors of electricity.

These properties of acids are characteristic and are made use of in testing for them.

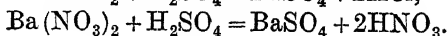
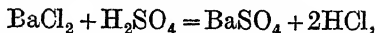
Preparation of Acids

1. Dissolve an acidic oxide in water. We have already seen that sulphurous acid and phosphoric acid can be made by this method.

2. When a salt of a volatile acid is heated with sulphuric acid, the volatile acid is driven off in the form of vapour and can be condensed. This does not mean that sulphuric acid is chemically 'stronger' than the other. In such a mixture two acids are present, sulphuric acid and the volatile acid combined with a metal. Sulphuric acid has the higher boiling point, so when the mixture is boiled the volatile acid is driven off first. Hydrochloric and nitric acids are made by this method. The equation for the action of sulphuric acid on sodium nitrate is .

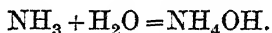


3. An acid may be prepared by the method of **Precipitation** or **Double Decomposition**. When dilute sulphuric acid is added to a solution of a salt of barium, barium sulphate, a very insoluble substance, appears as a fine powder called a **Precipitate**, which after a time settles, leaving the solution above clear. This is filtered off and the filtrate contains the acid which was combined with the barium.



Thus barium chloride gives a solution of hydrochloric acid and barium nitrate a solution of nitric acid. The quantity of sulphuric acid added must be exactly that required to combine with the barium, in order that the required acid may be obtained pure. A reaction of this kind is called a double decomposition, as both substances are broken up and exchange partners.

Alkalies. The chief alkalies are potassium hydroxide or caustic potash, KOH, potassium carbonate, K_2CO_3 , sodium hydroxide or caustic soda, NaOH, sodium carbonate, Na_2CO_3 , and ammonium hydroxide, NH_4OH . Potassium and sodium hydroxides and carbonates are solids which dissolve readily in water and give strongly alkaline solutions which turn litmus blue. Hence potassium and sodium are called the 'alkali metals.' Ammonium hydroxide is not known in the solid state. It is obtained in solution when ammonia gas is dissolved in water.



It is a powerful alkali and both the gas and the solution turn litmus blue.

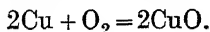
Properties of Alkalies

1. They have a bitter taste, but different from the taste of an acid.
2. They turn litmus blue.
3. They are good conductors of electricity.
4. A solution of caustic potash or soda has a soapy feel when rubbed between the fingers, and has a corrosive action on the skin, hence the name 'caustic' which means 'burning.'

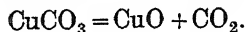
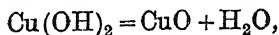
Bases. An alkali is a base which is soluble in water, but many bases are insoluble in water and are consequently not alkalies. We have seen that the metallic oxides are called 'basic' oxides. The term probably originated from the fact that most salts when heated decompose, leaving an oxide which is not further altered by heat and which the old chemists regarded as the basis or chief ingredient of the substance. The word base is usually applied to the oxides and hydroxides of the metals.

Preparation of Bases

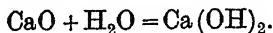
1. A basic oxide may be prepared by heating the metal in oxygen. *Example* : copper oxide :



2. It may be prepared by heating the hydroxide or carbonate of the metal. *Examples* : copper hydroxide and carbonate :



3. A few basic oxides dissolve in water and unite with it, giving soluble hydroxides or alkalies. *Example* : calcium oxide :



4. Insoluble hydroxides are made by precipitation. The method employed is to add sodium hydroxide or ammonium hydroxide to a solution of a salt of the metal. If the hydroxide is insoluble it will be precipitated.

EXPT.—Prepare some copper hydroxide by making a strong solution of copper sulphate in a beaker, and adding sodium hydroxide solution to the liquid (which must be cold) till no further precipitate appears. Filter it. Scrape the precipitate off the paper, transfer it to a crucible and heat over the Bunsen, gently, until it is dry, then more strongly. The residue is black copper oxide.

EXPT.—Repeat the experiment with copper carbonate prepared in the same way, but using sodium carbonate instead of sodium hydroxide.

EXPT.—Take a little of each of the following solutions in a test tube (one at a time), zinc sulphate, ZnSO_4 , ferric chloride, FeCl_3 , copper sulphate, CuSO_4 , and add drop by drop ammonium hydroxide, NH_4OH . Finally add a large quantity or 'excess.'

Zinc sulphate gives a white precipitate.

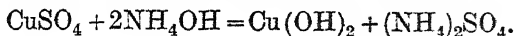
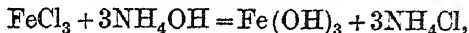
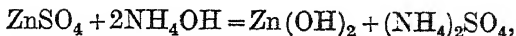
Ferric chloride gives a brown precipitate.

Copper sulphate gives a blue precipitate.

When ammonium hydroxide is added to copper sulphate solution, a blue precipitate is first formed, but when 'excess' of ammonium hydroxide is added the precipitate dissolves and a dark blue solution is left. The precipitate is said to be soluble in excess of ammonium hydroxide. This reaction is used as a test to shew the presence of copper in a solution.

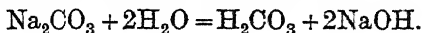
Repeat the experiment, using sodium hydroxide. How does the zinc hydroxide behave in this case ? This is also a common

test for zinc. The equations for the formation of the hydroxide are :

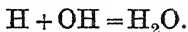


These reactions are all examples of double decomposition.

Note that hydrogen is contained in the formulae of acids which have been given. All acids contain hydrogen, and to it they owe their peculiar properties. In the formulae of hydroxides again, observe the presence of the group OH, which is known as 'hydroxyl.' All hydroxides contain this group. The alkaline carbonates, though in the solid state their formulae do not contain hydroxyl, when dissolved in water react with it, giving the OH group which is characteristic of hydroxides and alkalies. This action is called **Hydrolysis**, a term which means 'decomposition by water.'

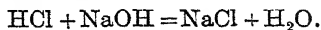


Neutralisation. An acid and an alkali when mixed in the proper proportions destroy one another. The hydrogen of the acid and the hydroxyl of the alkali unite to form water, thus :



This is the essential and important part of the reaction. The solution has then no acid or alkaline taste, and does not colour litmus either red or blue. When it is evaporated to dryness, a substance is obtained which has neither acid nor alkaline properties and is called a salt. This reaction is known as **Neutralisation**. Notice that it is the opposite of **Hydrolysis**.

Expt.—Take 50 c.c. of dilute hydrochloric acid, HCl, in a porcelain basin and add to it a few drops of litmus solution, giving a bright red colour. Then add sodium hydroxide solution, NaOH, till the colour changes to blue, the solution is then alkaline. Add the dilute acid very carefully drop by drop, till the liquid just loses its blue colour and does not become bright red. This is the neutral point, and the solution is now neither acid nor alkaline, it is neutral. Evaporate the liquid to dryness. A white substance is obtained (it may be slightly coloured by the litmus), which is common salt or sodium chloride, NaCl.



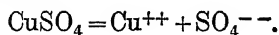
Salts. Sodium chloride is one of the large class of substances known as Salts, many of which we have already studied. The last experiment gives one way of making a salt. There are other methods which we shall consider later. A salt may be defined as 'a compound which is produced by replacing all or part of the hydrogen in an acid by a metal.'

A salt consists normally of two parts, known as **Radicals**. The first part, that is the metal, is called the positive or metallic radical, the second the negative or acid radical. In sodium chloride, NaCl, Na is the positive and Cl the negative radical. In Na_2CO_3 , Na_2 is the positive or metallic radical and CO_3 is the negative or acid radical. In acids, hydrogen is the positive, and the rest of the acid the negative radical. Hydrogen in its chemical behaviour often resembles the metals, so acids may be considered as salts of hydrogen. In hydroxides, the metal is the positive radical and the OH group the negative radical.

Ionization. Many compounds, acids, bases, and salts which dissolve in water, are in solution divided or dissociated into parts called Ions, the process being called Ionization. These ions may be single atoms or groups of atoms. Frequently they are identical with the radicals. Each ion carries an electric charge. If the positive radical becomes an ion it carries positive electricity, the negative radical carries negative electricity. The number of unit charges which each carries is equal to its valency. When sodium chloride is dissolved in water it is ionized thus :



Copper sulphate ionizes :



The sodium ion carries 1 unit charge because the valency of the sodium atom is 1. The copper ion carries 2 unit charges because the valency of the copper atom is 2.

When an electric current passes through such a solution the positively charged ions are attracted to the negative pole or **Cathode**, according to the usual electrical rule, and the negatively charged ions are drawn to the positive pole or **Anode**. On arriving at the cathode or anode, they give up to them their electric charges and become electrically neutral. In this way the ions act as carriers of the current. they carry positive elec-

tricity to the cathode and negative electricity to the anode. If a liquid contains no ions it is not a conductor. Pure water is a bad conductor because it is very slightly ionized; the addition of dilute sulphuric acid, which is highly ionized, provides the current carriers.

Following is given a table of some of the commoner elements which act as positive radicals in salts, and travel to the cathode in electrolysis. They are all metals, with the exception of hydrogen and ammonium. The valency or number of unit negative charges of the principal negative radicals is also given. Observe that the negative radicals may be single atoms or groups of atoms. One positive radical, ammonium, is a group of atoms. Such a group is called a compound radical, and enters into combination and is ionized as a unit.

Table of Radicals and Ions

Showing valency and number of unit charges.

Positive Radicals.		Negative Radicals.	
Valency 1	$\left\{ \begin{array}{l} \text{H}^+ \text{ Hydrogen} \\ \text{Na}^+ \text{ Sodium} \\ \text{K}^+ \text{ Potassium} \\ \text{NH}_4^+ \text{ Ammonium} \\ \text{Ag}^+ \text{ Silver} \\ \text{Hg}^+ \text{ Mercurous} \end{array} \right.$	Valency 1	$\left\{ \begin{array}{l} \text{OH}^- \text{ Hydroxide} \\ \text{Cl}^- \text{ Chloride} \\ \text{Br}^- \text{ Bromide} \\ \text{I}^- \text{ Iodide} \\ \text{NO}_3^- \text{ Nitrate} \\ \text{ClO}_3^- \text{ Chlorate} \end{array} \right.$
	$\left\{ \begin{array}{l} \text{Ca}^{++} \text{ Calcium} \\ \text{Ba}^{++} \text{ Barium} \\ \text{Mg}^{++} \text{ Magnesium} \\ \text{Zn}^{++} \text{ Zinc} \\ \text{Fe}^{++} \text{ Ferrous (iron)} \\ \text{Cu}^{++} \text{ Copper} \\ \text{Hg}^{++} \text{ Mercuric} \\ \text{Pb}^{++} \text{ Lead} \\ \text{Sn}^{++} \text{ Stannous (tin)} \end{array} \right.$		$\left\{ \begin{array}{l} \text{SO}_4^{--} \text{ Sulphate} \\ \text{S}_2\text{O}_3^{--} \text{ Thiosulphate} \\ \text{SO}_2^{--} \text{ Sulphite} \\ \text{S}^{--} \text{ Sulphide} \\ \text{CO}_3^{--} \text{ Carbonate} \\ \text{O}^{--} \text{ Oxide} \end{array} \right.$
	$\left\{ \begin{array}{l} \text{Fe}^{+++} \text{ Ferric (iron)} \\ \text{Al}^{+++} \text{ Aluminium} \\ \text{As}^{+++} \text{ Arsenic} \\ \text{Sb}^{+++} \text{ Antimony} \\ \text{Bi}^{+++} \text{ Bismuth} \end{array} \right.$		Valency 3 PO_4^{---} Phosphate
	Valency 4 Sn^{++++} Stannic (tin)		
	Valency 5 $\left\{ \begin{array}{l} \text{As}^{+++++} \text{ Arsenic} \\ \text{Sb}^{+++++} \text{ Antimony} \end{array} \right.$		

Valency of Elements generally found in Acid Radicals

Element	Valency.
Chlorine - - - -	- 1
Bromine - - - -	- 1
Iodine - - - -	- 1
Oxygen - - - -	- 2
Sulphur - - - -	- 2, 4, or 6
Nitrogen - - - -	- 3 or 5
Phosphorus - - -	- 3 or 5
Carbon - - - -	- 4

With the assistance of these tables it is easy to write the formula of a salt if we know its chemical name. In sodium chloride, the positive radical sodium, Na, has valency 1, and the negative chloride radical, Cl, has also valency 1; one atom of sodium thus unites with one atom of chlorine, giving the molecular formula NaCl. In zinc chloride, zinc has valency 2, therefore the zinc atom unites with two chloride radicals, and the formula becomes ZnCl_2 . In potassium sulphate, the sulphate radical SO_4 has valency 2, so it unites with two monovalent potassium atoms, giving K_2SO_4 . Ferric sulphate is a little more difficult. The ferric radical is trivalent, and the sulphate radical divalent. The rule is that the number of positive bonds must be equal to the number of negative bonds. If we take 2 ferric atoms we get 6 positive bonds, and taking 3 sulphate radicals we get 6 negative bonds. Therefore the formula of ferric sulphate is $\text{Fe}_2(\text{SO}_4)_3$. What is the formula of calcium phosphate? The calcium atom, Ca, is divalent and PO_4 , the phosphate radical, is trivalent. Multiplying Ca by 3 and PO_4 by 2, we get 6 positive and 6 negative bonds, and the formula is $\text{Ca}_3(\text{PO}_4)_2$.

The formula of ferric sulphate might be written $\text{Fe}_2\text{S}_3\text{O}_{12}$, and that of calcium phosphate $\text{Ca}_3\text{P}_2\text{O}_8$, but in order to shew the radicals clearly, we place them in brackets and write the coefficient outside, thus: $\text{Ca}(\text{OH})_2$, $\text{Fe}_2(\text{SO}_4)_3$, $\text{Ca}_3(\text{PO}_4)_2$.

QUESTIONS

1. State any two chemical properties which distinguish the metallic from the non-metallic elements. Illustrate your answer by referring to two typical members of each class.

(Scot Leaving Cert.)

2. If an unknown element were given to you, and you were asked to find out whether it should be classified as a metal or non-metal, how would you proceed ? (Scot. Leaving Cert.)

3. Give four general methods of preparing acids, illustrating each method by two examples. (London Matric.)

4. What do you understand by the terms: basic oxide, anhydride, peroxide, acid ? Give examples. (London Matric.)

5. What are the principal characteristics of acids, bases, and salts ? State briefly, giving one example with the equation in each case, how you would prepare :

An acid, (a) from an element, (b) from a salt.

A base, (a) from an element, (b) from a salt.

Give also, with equations, two methods of preparing salts. (Scot. Leaving Cert.)

6. Give a general but concise account of the phenomena which occur when a salt is dissolved in water and the solution is electrolysed. Describe briefly two instances of the practical application of electrolysis. (London Matric.)

CHAPTER XVII

CARBON

WE will now consider a solid non-metallic element, Carbon. Carbon is an important constituent of the substance of all animals and plants. It is found in minerals, chiefly in combination with oxygen and metals in carbonates, but also in the uncombined state. The element exists in nature in two crystalline forms: first, the rare and valuable Diamond; second, the commoner and cheaper Graphite.

The diamond is found in South Africa, India and Brazil. In its natural state it is a slightly yellow, dull-looking pebble. To reveal its beauty and sparkle it must be cut and polished by the diamond cutter, and is then sometimes known as a *brilliant*. The glitter and sparkle of the diamond is due to its exceptional power of reflecting and refracting light. It is rather brittle and is the hardest of all known substances. The hardness of a substance is usually measured by its ability to scratch other materials, and the corner of a diamond crystal will scratch any smooth surface. It is used for cutting glass, and inferior stones such as black diamonds, which are useless as gems, are employed for drilling rocks and for cutting and polishing other stones.

We have seen that carbon burned in oxygen gives carbon dioxide gas. A diamond can be burned in oxygen, and is found to give the theoretical quantity of carbon dioxide which would be produced by burning an equal weight of carbon. This is a proof that diamond consists of pure carbon.

The second crystalline variety of carbon is Graphite. Graphite is a soft black mineral, found in Britain in Cumberland, in Ceylon, America and many other places. Graphite makes a black mark on paper and is used, mixed with fine clay, for making lead-pencils. For a very black and soft pencil the

mixture is mainly graphite, for a hard pencil giving a light mark the proportion of clay is increased. Metallic lead also marks paper, and graphite was formerly supposed to contain lead and was called plumbago, from *plumbum*, the name for lead. So-called 'lead-pencils' do not contain lead. As 'black-lead' graphite is used for protecting iron grates and stoves from rusting. It is also used for lubricating machinery.

Graphite burns in oxygen, giving carbon dioxide. Neither diamond nor graphite dissolves in acids, and they are unaffected by most chemical reagents. Though these two substances have exactly the same chemical composition, their physical properties could not well be more different. Draw your own comparisons.

There are also artificially prepared non-crystalline or amorphous varieties of carbon. The chief of these are Charcoal, Coke and Lampblack.

When wood is burned it is completely consumed, leaving only a grey ash. If it is heated in a tube containing a limited quantity of air, it is blackened or charred. An inflammable gas is given off, moisture condenses on the cooler part of the tube, and a residue of Charcoal is left. This is carbon, but is impure, as it still contains ash.

EXPT.—Place some pieces of wood in a hard glass test tube. Clamp it horizontally on a retort stand and fix up a leading tube to collect the gas over water. Heat the tube till the wood is converted into charcoal. Test the liquid for acidity with litmus paper, and the gas for inflammability with a lighted taper. The liquid contains acetic acid or vinegar and the gas consists mainly of hydrogen, carbon dioxide and carbon monoxide. Transfer the residue of charcoal to a crucible and heat openly till only ash is left.

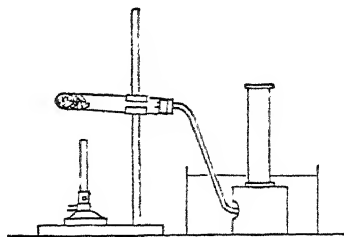


FIG 51.

Charcoal is very porous and can absorb large quantities of gases.

EXPT.—Heat gently a little strong ammonia solution in a flask, ammonia gas is given off. Dry the gas by passing it through a U-tube containing quicklime (the usual drying agents, calcium

chloride and strong sulphuric acid, absorb ammonia), and collect some of it in a gas jar over mercury. As the gas is very soluble it

cannot be collected over water. Remove the leading tube. Heat a piece of charcoal in a closed crucible to expel air, and pass it up into the ammonia. The mercury level will rise as the gas is absorbed. Hard wood charcoal absorbs 90 times its own volume of ammonia. Nut charcoal works well.

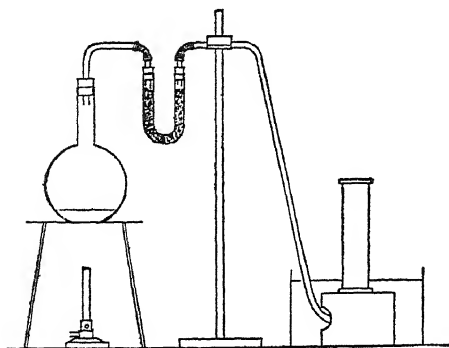


FIG 52.

Charcoal also absorbs solid and liquid bodies. It is used in refining sugar to re-

move the brown colouring matter, and in filters to purify water. Animal charcoal made from bone is best.

Coke is derived from coal by heating it in closed retorts.

EXPT.—Repeat the experiment for making charcoal, but use coal instead of wood. The products are, an alkaline liquid (test with litmus paper), coal tar and coal gas, the residue is Coke.

Coal gas is made in gas-works by heating coal in fireclay retorts, and contains up to 50% of hydrogen with other gases. The coke is a by-product, that is, the main object of the process is gas-making. Coke is a valuable fuel. It contains about 50% of carbon, and is largely used in the manufacture of iron and other metals. Carbon, like hydrogen, is a reducing agent. When it is heated with a metallic oxide it combines with the oxygen to form carbon dioxide, and this sets free the metal.

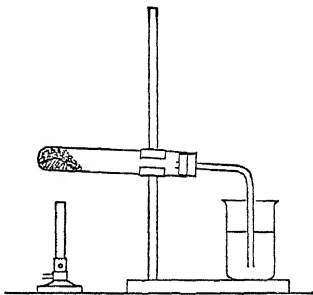
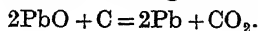


FIG. 53

EXPT.—Powder some coke and mix it with a little oxide of lead or litharge. Place the mixture in a hard glass tube and heat.



In order to shew that CO_2 is formed, the tube may be connected to a leading tube which dips into lime water. Allow to cool and empty the contents of the tube into a basin of water, the heavier lead remains at the bottom, and the lighter carbon can be washed away.

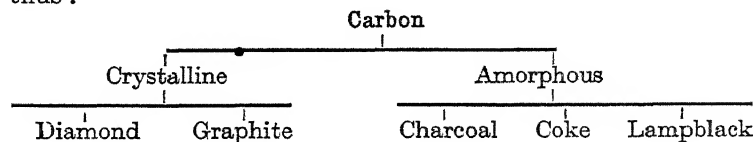
Lampblack is a kind of soot, made by burning oil, turpentine or tar in a limited supply of air. It is one of the purest kinds of artificially prepared carbon, and is used in making printers' ink and paints.

Coal is a natural product consisting mainly of carbon. Geologists tell us that it has been formed by the decay of vegetable matter and solidified by great pressure. Peat is the first stage in this transformation, then brown coal or lignite, then ordinary house coal or bituminous coal, and finally anthracite which is hard and smokeless. Ordinary coal contains 70%-80% of carbon, as well as small quantities of oxygen, hydrogen, nitrogen and sulphur, in combination. When burned it leaves a mineral ash.

When water is boiled it vaporises and can be condensed. It distils without any change of composition. When coal is heated in a retort it is not changed bodily into a gas, but is decomposed, giving gas and a residue of solid. This process is consequently called 'destructive' distillation, and is employed in gas-works for the manufacture of illuminating gas. It is a chemical change; ordinary distillation is a physical change.

Tar is a very important by-product of gas-making. The following are a few of the substances which can be obtained directly or indirectly from coal tar: Aniline dyes, of which there are thousands of shades. Creosote, used for preserving wood. Explosives, such as T.N.T. Disinfectants, like carbolic acid. Perfumes. Drugs, as aspirin and antipyrin, and saccharin, which has 300 times the sweetening power of sugar.

Carbon is an example of allotropy as it can exist in three allotropic forms, the crystalline diamond, the different crystalline form of graphite, and the amorphous state of charcoal and coke. The various kinds of carbon may be tabulated thus:



Additional Experiments

EXPT.—Boil some indigo solution with animal charcoal, filter, and note that the liquid is decolorised.

EXPT.—Heat some bone in a test tube and show that litmus paper gives an alkaline reaction.

EXPT.—Make sugar charcoal by heating sugar in a test tube.

EXPT.—Heat a mixture of copper oxide and powdered charcoal in a hard glass tube to obtain metallic copper.

EXPT.—Oxides of copper, lead, silver, bismuth, and antimony may be reduced to the metallic state by mixing with sodium carbonate and heating on a block of charcoal with a blowpipe.

QUESTIONS

1. Describe briefly the allotropic forms of carbon. Describe experiments to illustrate the use of charcoal for absorbing gases and for decolorising certain liquids. How would you determine the percentage of combustible matter in the 'lead' of a lead pencil ? (London Matric.)

2. How could you shew that graphite is an allotropic form of carbon ? Mention one other element which occurs in allotropic forms and describe the preparation and appearance of each form. (Oxford and Camb. School Cert.)

3. How can charcoal be converted into graphite and diamond ? What experiments would you make in order to shew that the three substances contain only the same element ? (London Matric.)

4. What elements are contained in coal ? Describe as fully as you can what happens when coal burns in an ordinary fire.

5. Write a short paragraph (50-100 words) on 'Coal.' What are the respective substances known as charcoal, animal charcoal, coke, and lampblack ? (Scot. Univ. Entrance.)

6. Red oxide of mercury is heated (1) alone, (2) with carbon, (3) with hydrogen. What products are formed, and what weight of each would be obtained, if 10 grams of mercuric oxide were used ? (London Matric.)

7. Carbon is a reducing agent. Give two examples of its use in obtaining the metal from a metallic oxide. Mention another reducing agent which could be used for the same purpose.

CHAPTER XVIII

CARBON DIOXIDE

THE symbol of carbon is C, and its atomic weight is 12. It is a tetravalent element, that is, the atom has 4 hooks or bonds. Using all these bonds, one atom of carbon unites with two atoms of oxygen to form Carbon Dioxide, CO_2 . We may write the formula thus, $\text{O}=\text{C}=\text{O}$, representing each valency bond by a dash. This is known as a graphic formula and enables us to form a clearer mental picture of the structure of substances. Similarly, the formula of water becomes $\text{H}-\text{O}-\text{H}$, and ferric oxide is $\text{O} \begin{array}{c} \diagup \text{Fe}=\text{O} \\ \diagdown \text{Fe}=\text{O} \end{array}$. We must not assume that a graphic formula represents in every case the actual grouping of the atoms, it is merely a picture which helps us to understand better the formation and decomposition of chemical compounds.

If the carbon atom uses only two of its four bonds it forms with oxygen Carbon Monoxide, CO , or $=\text{C}=\text{O}$. Carbon monoxide has thus still some combining power, and we shall see that it burns readily in air, taking up another atom of oxygen to form the dioxide.

History. A description has already been given of the experiment carried out by Van Helmont with a growing tree, which seemed to shew that its substance was derived entirely from water. We now know, however, that plants require for their growth not only water but carbon dioxide, which they extract from the atmosphere. Yet it was Van Helmont who discovered carbon dioxide. He observed that when limestone and acid were enclosed in a tightly corked bottle, the bottle was burst by the pressure of the gas produced. To this gas he gave the name 'gas sylvestre' or 'gas of the woods,' because it seemed to him a 'wild untameable' substance. Joseph

Black (1754) found that carbon dioxide combines with bases to form salts and called it 'fixed air.' Lavoisier (1783) shewed that it is an oxide of carbon and determined its composition by burning charcoal and diamond in oxygen.

Occurrence. Carbon dioxide is present in the atmosphere to the extent of about 3 volumes in 10,000. It rises from the ground in certain places, such as the Grotta del Cane or the Dog's Grotto, near Naples. The gas is heavier than air, and remains as a layer on the ground about 18 inches deep, so that if a man and a dog enter the cave, the dog is suffocated while the man can breathe freely. Carbon dioxide is found in many mineral waters. It is produced during respiration, and is a product of fermentation, of the decay of organic matter, and of the combustion of fuel.

Preparation. All carbonates give off carbon dioxide when acted upon by acids. It is most conveniently made from calcium carbonate (marble chips) and dilute hydrochloric acid.



The gas may be prepared in a Kipp, or in a flask fitted with a leading tube, and collected by downward displacement, as it is heavier than air.

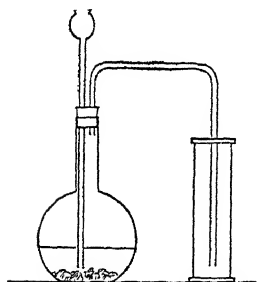


FIG. 54.

EXPT.—Fit up a flask with thistle funnel and delivery tube. The tube is bent twice at right angles and dips into a gas jar. Put some pieces of marble in the flask and pour in dilute hydrochloric acid through the funnel till they are covered. The jar is full when a lighted taper held in its mouth is extinguished. Collect 4 or 5 jars for use in the following experiments, and cover them with greased glass plates.

EXPT.—Lower a lighted taper into a jar. It is immediately extinguished. Carbon dioxide is not inflammable and does not support combustion.

EXPT.—Arrange an experiment as shewn. *A* is a small oblong trough in which several short pieces of lighted candle are placed. *B* is a gutter made of stiff cardboard, resting on the edge of the trough and supported by a stand. Pour down a large jar of carbon

dioxide in the gutter, it flows like water, fills the trough and extinguishes the candles. This experiment shews that carbon

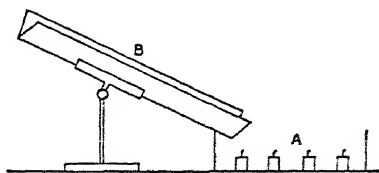


FIG 55.

dioxide is heavier than air, that it does not support combustion and consequently extinguishes flame.

EXPT.—Place an empty beaker on the pan of a balance and counterpoise it, that is, add weights to the other pan until it is exactly balanced. Pour carbon dioxide into the beaker. The result shews that carbon dioxide is heavier than air.

EXPT.—By means of a piece of string lower a small beaker into a jar of the gas. Draw it up and empty it into another jar. By repeating this several times the gas can be transferred from one jar to the other. Test each with a lighted taper.

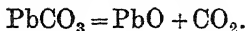
Most metallic carbonates are decomposed when heated to a red heat, giving the oxide of the metal and carbon dioxide.

EXPT.—Heat some lead carbonate in a test tube provided with a leading tube and collect the gas. Test it for carbon dioxide.

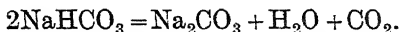
Potassium and sodium carbonates are not decomposed when heated.

EXPT.—Heat some sodium carbonate in a test tube and test for carbon dioxide.

The equation for the decomposition of lead carbonate is



Pure carbon dioxide can be prepared by heating sodium bicarbonate.

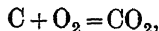


When carbon or any of its compounds burns in excess of air or in oxygen, carbon dioxide is produced. It is sometimes called Carbonic Acid Gas, as it is an acidic oxide and its solution in water reddens litmus paper.

Properties. Carbon dioxide is colourless and odourless, it has an acid taste. It is half as heavy again as air. Verify this by calculation from the molecular weights. It can be liquefied by pressure and is stored in iron cylinders. When the liquid is allowed to flow out of a cylinder, it evaporates, and the cold thus produced freezes it into a snow-like substance, solid carbonic acid. A mixture of solid carbon dioxide and ether is an excellent freezing mixture. It gives a temperature of -75° , and easily freezes mercury.

Carbon dioxide at ordinary pressure and temperature dissolves in its own volume of water. Soda water is merely water with carbon dioxide dissolved in it at a pressure of 3-4 atmospheres. When a bottle of aerated water is uncorked, the pressure is released and the gas comes out of solution, causing effervescence. Carbon dioxide is produced during the process of fermentation. The 'raising' of bread and its porous structure are due to the formation of carbonic acid gas by the fermenting action of the yeast. Baking powder consists of bicarbonate of soda and tartaric acid. When these solids interact in the presence of water, carbon dioxide is evolved. Seidlitz powders, health salts and such medicines are composed of similar substances. Fire extinguishers frequently contain an acid and a carbonate which can be brought in contact when required to give a stream of carbonic acid gas.

Carbon dioxide is not actually a poisonous gas, but when breathed it causes suffocation, as it deprives the lungs of oxygen. Air containing 1 part of carbon dioxide in 500 is injurious, and 20% in the atmosphere would cause death. We take oxygen from the air into our lungs, whence it is carried by the blood to oxidize the waste material (mainly carbon compounds) of the body. The oxygen oxidizes the carbon to carbon dioxide,



which is taken back to the lungs and breathed out again. It is this slow process of oxidation which provides the heat of the body.

EXPT.—Pour a little lime water into a test tube. Insert in the tube a 12-inch piece of glass tubing. Take a deep breath and blow gently through the lime water till it turns milky, indicating the presence of carbon dioxide.

Green plants, on the other hand, in the presence of sunlight absorb carbon dioxide from the air, extract the carbon and give back the oxygen.

EXPT.—Fill a jar with water which has been saturated with carbon dioxide by bubbling the gas through it for some time. Put into the jar some fresh watercress and invert it in a trough of water. If it is placed in bright sunshine, bubbles of gas rise and collect in the jar. This is oxygen, but may contain some carbon dioxide. To remove this, extract the greenstuff, slip a piece of caustic soda up into the jar and close it with a greased plate. Remove from the trough and stand for a short time, shaking occasionally. The sodium hydroxide solution absorbs any carbon dioxide. If the quantity of gas is small, transfer it to a test tube under water, and test with a glowing wood splinter for oxygen.

The Carbon Dioxide Cycle. Carbon dioxide is absorbed by green plants and dissolved by the sea, and some rocks combine with it chemically. It is supplied by respiration, combustion and decay of organic matter. These processes of demand and supply almost balance each other, so that the quantity of carbon dioxide in the atmosphere remains practically constant.

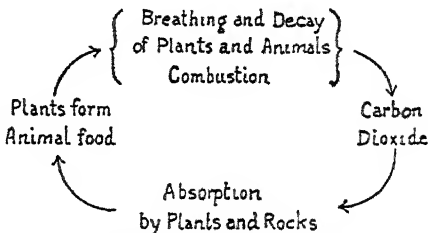
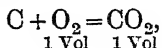


FIG. 56 —Carbon Dioxide Cycle.

Composition. That carbon dioxide contains carbon and oxygen can be shewn by the following experiment.

EXPT.—Fill a gas jar with carbon dioxide. Light a piece of magnesium ribbon and lower it at once into the gas. It continues to burn, giving white magnesium oxide and black particles of carbon. Examine the oxide to satisfy yourself that it is the same as is obtained when magnesium is burned in oxygen. Dissolve it in dilute hydrochloric acid, a black residue of carbon is left. This may be burned in oxygen as in a former experiment, and the gas tested with lime water.

Volume Composition. When carbon combines with oxygen, one volume of oxygen gives one volume of carbon dioxide,



so the volume of gas remains unchanged.

EXPT —Take a large hard glass test tube and fit it with a two hole rubber stopper. In one hole insert a piece of glass tube, *A*,

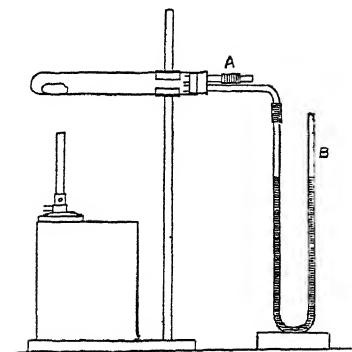


FIG. 57.

carrying an inch of rubber tubing, which can be closed by means of a piece of glass rod. A tube passing through the other hole connects with a manometer, *B*. Before placing the mercury in the manometer drop a piece of charcoal into the tube, and pass through *A* a quick current of oxygen to sweep out the air. Replace the plug in *A*, pour mercury into *B*, and take out the plug for a moment to equalise the pressure. Heat the carbon till it burns. The gas expansion due to heat will first depress the mercury in the nearer limb, but when the apparatus has cooled the

levels will be the same, shewing that the volume of carbon dioxide produced equals the volume of oxygen consumed.

One volume of carbon dioxide contains one volume of oxygen;

\therefore 1 molecule of carbon dioxide contains 1 molecule of oxygen.

The molecule of oxygen contains 2 atoms, therefore the molecule of carbon dioxide contains 2 atoms of oxygen, and its formula is C_xO_2 , where x is a small whole number.

The relative density of carbon dioxide is 22.

Its molecular weight is consequently 44, which contains 32 parts of oxygen and 12 parts of carbon.

The weight of 1 atom of carbon is 12 ;

\therefore the formula of carbon dioxide is CO_2 .

The manometer is a piece of glass tube bent into a U shape, and partly filled with mercury. It is used for measuring pressure. When the pressure in both limbs is the same, the mercury levels of course coincide. When the pressure in one limb increases the mercury is depressed, and the pressure in that limb is then the barometric pressure plus the difference in height between the mercury levels in the manometer.

Tests for Carbon Dioxide. 1. Pass the gas through lime water or pour it into a test tube containing lime water and shake. The liquid turns milky.

2. Introduce a burning taper into the gas, the flame is immediately extinguished.

Estimation of Carbon Dioxide. When carbon dioxide is passed through a solution of sodium or potassium hydroxide, it is readily absorbed.

EXPT.—Collect a little carbon dioxide in a tube over mercury. Introduce by means of a bent pipette a few c.c. of sodium hydroxide solution. Note that the mercury gradually rises in the tube, shewing that the gas is being absorbed.

This reaction is made use of in the estimation of carbon dioxide. A mixture of gases containing carbon dioxide is measured, then passed through sodium hydroxide solution and remeasured. The difference of volume represents the volume of carbon dioxide.

Additional Experiments

EXPT.—To shew the absorption of carbon dioxide by caustic soda. Take a glass tube 9 or 10 inches long, and $\frac{3}{4}$ -inch in diameter. Clamp this in a sloping position with the lower end under water, and the upper end closed by a one hole rubber stopper carrying a dropping funnel. Fill the tube quickly with carbon dioxide with the stop-cock open. Close the stop-cock and pour some caustic soda into the funnel. Then admit the soda drop by drop, and observe the rise of the water in the tube.

EXPT.—Fix pieces of candle to the inside of a wide cylinder at different heights. Light them, and lead in carbon dioxide. Note how they become successively extinguished as the level of the gas rises.

EXPT.—Pour a little benzene or petroleum into a dish. Light it and pour in a beaker of carbon dioxide.

EXPT.—If a carbon dioxide cylinder is available, obtain some solid carbon dioxide by wrapping a towel loosely round the outlet and opening the tap. Show the freezing of mercury. Line a porcelain basin with paper and place in it some mercury. Insert into the mercury a stout copper wire bent at the end, to lift out the solid. Cover the mercury with solid carbon dioxide and moisten with ether. Lift out the mercury when frozen and show its solidity. If quickly suspended in water in a beaker it becomes covered with a layer of ice. The mercury melts first, then the ice.

QUESTIONS

1. How is carbon dioxide usually prepared ? State clearly your reasons for regarding it as a compound of the two elements, carbon and oxygen, and describe an experiment by which you could shew that the gas contains its own volume of oxygen.

(London Matric.)

2. How could you prove that the gas evolved on pouring dilute hydrochloric acid on chalk is the same as that obtained when chalk is strongly heated ?

3. A certain weight of marble is dissolved in dilute hydrochloric acid, and 288 c.c. of carbon dioxide measured at 15°C . and 760 mm. are evolved. What weight of marble was used ?

4. Write an explanatory note on (a) the effervescence which takes place when a bottle of lemonade is opened, (b) the use of yeast in bread-making.

(Scot. Leaving Cert.)

5. Give an account of the Carbon Dioxide Cycle in Nature, and describe the part which carbon dioxide plays in the life processes of animals and plants.

CHAPTER XIX

CARBONATES. ACID, NORMAL AND BASIC SALTS. SOFT AND HARD WATERS

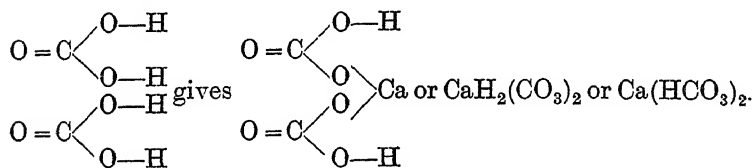
CARBON dioxide enters into the composition of the salts known as **Carbonates**, and generally speaking, a carbonate consists of a metallic oxide united with carbon dioxide. Salts are produced by replacing the hydrogen part of acids by a metal. The common acids may contain one, two, or three atoms of hydrogen in the molecule, *e.g.* hydrochloric acid, HCl , sulphuric acid, H_2SO_4 , phosphoric acid, H_3PO_4 . If we replace the hydrogen atom in HCl by the monovalent sodium atom we can only get one chloride, NaCl . Replacing the hydrogen of H_2SO_4 by the sodium atom, we can derive two sulphates, NaHSO_4 and Na_2SO_4 . The first of these is known as an **Acid Sulphate** because it still contains hydrogen, or as a **Bisulphate**, the second is the **Normal Sulphate**. Similarly we can derive from H_3PO_4 three phosphates, NaH_2PO_4 , Na_2HPO_4 , and Na_3PO_4 . These are called, respectively, sodium dihydrogen phosphate, indicating that the molecule contains two atoms of hydrogen; disodium hydrogen phosphate, showing that it contains two atoms of sodium; and normal sodium phosphate, in which all the hydrogen has been replaced by sodium.

Carbon dioxide is frequently called carbonic acid, but the term is more properly applied to the substance H_2CO_3 , which we presume is formed when carbon dioxide is dissolved in water, as acidic oxides unite with water to form acids. If an attempt is made to obtain the pure substance, H_2CO_3 , by evaporating the solution, it breaks up into H_2O and CO_2 , so that it has not been isolated and is consequently called a 'hypothetical' acid. If then we replace one or both atoms of the hydrogen of carbonic acid by one atom or two atoms of any monovalent metal, we can derive two carbonates. Thus with

sodium we get NaHCO_3 and Na_2CO_3 . NaHCO_3 is an acid carbonate but is generally called sodium bicarbonate or baking soda, and Na_2CO_3 is normal sodium carbonate, or simply, sodium carbonate. The crystalline form of sodium carbonate containing 10 molecules of water of crystallisation is known as washing soda. Di- and trivalent metals may also form acid salts, that is, salts containing hydrogen. Calcium, which is divalent, forms a normal and an acid carbonate. If we replace the two hydrogen atoms in H_2CO_3 by one atom of calcium, we get CaCO_3 , normal or common calcium carbonate. How then can we derive the acid salt or bicarbonate? We must take two molecules of the acid, and replace two hydrogen atoms by one atom of calcium.

H_2CO_3 gives CaCO_3 , usually written $\text{CaH}_2(\text{CO}_3)_2$ or $\text{Ca}(\text{HCO}_3)_2$.

If we write the graphic formulae this becomes clearer.



The calcium atom thus replaces one hydrogen atom in each molecule and binds the two together to form one molecule.

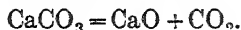
An acid which contains one hydrogen atom in its molecule, *e.g.* HCl , is called a **Monobasic Acid**. One which contains two hydrogen atoms, *e.g.* H_2CO_3 , is called a **Dibasic Acid**, and one which contains three hydrogen atoms like H_3PO_4 , is known as a **Tribasic Acid**. Many of these acid salts react acid to litmus, but this is not always the case; some are neutral and some actually alkaline.

In addition to normal and acid salts there are also **Basic Salts**. A salt may not only be derived from an acid by replacing hydrogen by a metal, but can also be derived from a hydroxide or base by replacing the OH group (characteristic of hydroxides) by a non-metal. Thus by replacing the OH group in sodium hydroxide, NaOH , by chlorine, we get only one salt sodium chloride, NaCl . If we replace the two OH groups in lead hydroxide, $\text{Pb}(\text{OH})_2$, by chlorine, we get lead chloride, PbCl_2 . But we can derive another salt by replacing

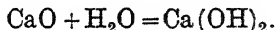
one OH by chlorine, $\text{Pb}(\text{OH})\text{Cl}$, and this is called basic lead chloride. These basic salts are usually insoluble in water.

The normal metallic carbonates are also as a rule insoluble; exceptions are sodium, potassium and ammonium carbonates. Carbonates are found extensively in nature as minerals. Calcium carbonate exists in several different forms, *chalk, limestone, marble, Iceland spar* and others. The mineral *magnesite* is magnesium carbonate, MgCO_3 , and the well-known rock, *dolomite*, is a double carbonate of calcium and magnesium, $\text{CaCO}_3 \cdot \text{MgCO}_3$.

When calcium carbonate is heated strongly it loses carbon dioxide and is converted into calcium oxide or quicklime:



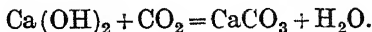
Quicklime is a white non-crystalline substance. When heated in the oxyhydrogen flame it gives out an intense white light known as limelight. If a little water is added to freshly burned quicklime, they unite to form calcium hydroxide or slaked lime:



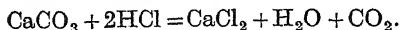
This is an exothermic reaction, and the heat given out is so great that part of the water may be converted into steam. Quicklime is made on a large scale by heating limestone in kilns. It is mixed with water and sand to make 'mortar.' This is used in building for filling in the joints between stones and bricks, and binds them strongly together.

EXPT.—Heat a gram or two of powdered calcium carbonate as strongly as possible in a porcelain crucible over a blast burner or a blowpipe for 20 minutes. Allow to cool. Add a few drops of water and note the rise of temperature. Transfer to a beaker. Add 100 c.c. of water. The calcium oxide is transformed into calcium hydroxide and some of it dissolves in the water. Do not heat, as the solubility decreases with rise of temperature. Allow to settle and filter the clear liquid. This is lime water, a solution of calcium hydroxide. It should be alkaline, so test with litmus paper. Add dilute hydrochloric acid, what does the absence of effervescence indicate?

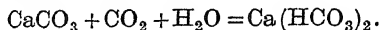
When carbon dioxide is passed through lime water a white precipitate of calcium carbonate is produced.



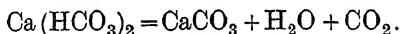
EXPT.—Take 50 c.c. of lime water in a beaker, pass through it for two minutes a stream of carbon dioxide. The liquid turns milky owing to the precipitated calcium carbonate. Add a little dilute hydrochloric acid. The liquid becomes clear, with effervescence; what does this prove?



EXPT.—Take 50 c.c. of lime water and pass through it a stream of carbon dioxide until the precipitate first formed dissolves again and the liquid clears. It now contains calcium bicarbonate, which is soluble in water.



Thus carbon dioxide in the presence of water converts the normal carbonate into the bicarbonate. Now heat the solution to boiling, the bicarbonate is decomposed, calcium carbonate is reprecipitated and carbon dioxide is given off. Observe that this is just the reverse of the preceding reaction.

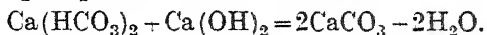


Soft and Hard Waters. In washing, when soap readily gives a lather or foam with water, the water is said to be 'soft.' Some waters, however, produce a lather only with difficulty and cause a considerable waste of soap. These are called 'hard' waters. Hardness is due to the presence of dissolved salts. Water in passing through the soil dissolves various substances. Thus spring or well water is usually hard, while rain and lake waters are soft. There are two kinds of hardness, 'temporary' and 'permanent.' Temporary hardness is so called because it can be removed by boiling, and is due to the bicarbonates of calcium and magnesium. When water containing dissolved carbon dioxide passes through soil containing the carbonates of calcium and magnesium (limestone and magnesite), it dissolves a little of these salts, forming the bicarbonates. When the water is boiled, these are decomposed, precipitating the normal insoluble carbonates. To this is due the crust or scale which forms inside kettles and boilers. Boiling does not remove permanent hardness, which is due to chlorides and sulphates of calcium and magnesium.

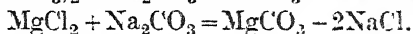
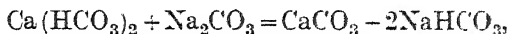
Soap consists of the sodium salts of the organic 'fatty' acids, palmitic, stearic, and oleic. These salts are soluble in water. If the water contains calcium or magnesium compounds in solution they react with the soap, giving the calcium

and magnesium salts of the fatty acids, which are insoluble in water and are precipitated, forming a 'curd.' It is only when these salts have been all precipitated that the solution of soap necessary for washing is obtained.

Temporary hardness may be removed by boiling or adding lime, which precipitates calcium carbonate.



Both kinds of hardness are removed by adding sodium carbonate, which precipitates calcium and magnesium as carbonates.



The total hardness of water is sometimes estimated by the use of soap solution. A little soap is dissolved in water and the solution added gradually to a measured quantity of the hard water, shaking vigorously after each addition till a permanent lather is obtained. The quantity of soap solution added is a measure of the total hardness.

The normal carbonates of the metals are mostly insoluble, and some of them have distinctive colours. These afford a means of testing for the metals by adding sodium carbonate to solutions of their salts. In each case a precipitate of the metallic carbonate is produced.

EXPT.—Take a little of each of the following solutions in separate test tubes and add sodium carbonate solution:

Calcium chloride	CaCl_2	gives a	white	precipitate.
Ferric chloride	FeCl_3	„	brown	„
Copper sulphate	CuSO_4	„	blue	„
Nickel sulphate	NiSO_4	„	green	„
Cobalt nitrate	$\text{Co}(\text{NO}_3)_2$	„	red	„
Chromium sulphate	$\text{Cr}_2(\text{SO}_4)_3$	„	grey green	„

Additional Experiments

EXPT.—Hardness of water. Prepare a standard solution of calcium chloride. Weigh exactly 0.4 gram of pure calcium carbonate or Iceland spar, and dissolve in 100 c.c. of roughly $\frac{\text{N}}{10}$ hydrochloric acid. Evaporate to dryness on the water bath, dissolve in water and make up to 2 litres. One c.c. of this solution corresponds to 0.2 milligram of calcium carbonate. Standard soap solution is made by dissolving 2 grams of Castile soap in a mixture

of 100 c.c. of alcohol and 100 c.c. of water. Measure 50 c.c. of the standard calcium chloride into a stoppered bottle and add the soap solution from a burette in small quantities, shaking vigorously after each addition, till a lather lasting 5 minutes is obtained. Dilute the soap solution by calculation, so that 14.25 c.c. gives a permanent lather with 50 c.c. of the standard calcium chloride. Hardness is expressed as parts of calcium carbonate per 100,000, and when 50 c.c. of a hard water requires 14.25 c.c. of standard soap solution, this means a hardness of 20 parts per 100,000. The hardness corresponding to the number of c.c. of soap solution used may be obtained by reference to a hardness table. Distilled water requires 0.7 c.c. of soap solution to give a lather.

EXPT.—Compare the hardness of the standard calcium chloride solution with distilled water, tap water, and any hard water you can obtain.

QUESTIONS

1. Explain the difference between carbonates and bicarbonates, illustrating your answer by reference to the corresponding salts of another acid. (Scot. Leaving Cert.)

2. Explain what is meant by the basicity of an acid. Give one example of a monobasic acid and one of a dibasic acid, and state clearly any experimental facts which justify the referring of these examples to their respective classes.

3. Give the formulae for washing soda and baking soda. How are these salts related chemically? How could you convert each into the other? Describe the function of baking soda as an ingredient of baking powder, and say what other ingredient is necessary. (Scot. Univ. Entrance.)

4. Explain clearly what is meant by a normal salt, an acid salt, and a peroxide, giving two examples of each. (London Matric.)

5. What is a hard water? Describe any experiment you have made which explains the fact that chalk, although practically insoluble in water, is deposited when some hard waters are boiled. What causes the hardness in certain waters which do not deposit chalk on boiling? How does sodium carbonate act upon hard water? (London Matric.)

6. Carbon dioxide is passed through lime water. How will the hardness of the water vary as the current of gas continues? How would you prove your statements experimentally? (Oxford and Camb. School Cert.)

7. Explain how a hard water is produced in nature, and give an account of the natural formations known as stalactites and stalagmites. (Scot. Univ. Entrance.)

CHAPTER XX

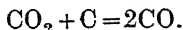
CARBON MONOXIDE. PRODUCER GAS. WATER GAS. CARBIDES

Carbon Monoxide

Occurrence and History. Carbon monoxide, CO, is not present as a constant constituent of the atmosphere. It was first prepared by Lassone (1776) by heating a mixture of charcoal and zinc oxide. Its composition was not then known, and it was called with other inflammable gases, 'inflammable air.' Cruickshank (1800) shewed that it was an oxide of carbon, and Dalton (1808) found that on combustion it gives carbon dioxide, combining with half its own volume of oxygen.

Preparation. When a coal fire has become red hot, blue flames may be seen on its upper surface; these are the flames of burning carbon monoxide. When carbon dioxide is passed through red hot-carbon it is reduced to carbon monoxide. It is supposed that oxygen entering at the bottom of the fire first unites with carbon to form carbon dioxide, which on passing through the glowing coke is reduced to carbon monoxide. Carbon monoxide is also formed when carbon is burned with a limited supply of air.

1. Take an iron tube, 18 inches long and $\frac{3}{4}$ -inch internal diameter, and pack it with small pieces of charcoal. Heat the tube to redness with a row of burners and pass through it a slow stream of carbon dioxide. Carbon monoxide is produced, which may be purified from carbon dioxide by passing through strong caustic soda solution, and collected over water.



2. The most convenient laboratory method of preparing the gas is by the action of concentrated sulphuric acid on one

of the following substances: formic acid, sodium formate, oxalic acid or potassium ferrocyanide.

EXPT.—Fit up the apparatus as illustrated. *A* is the generating flask, from which the gas, which consists of equal volumes of

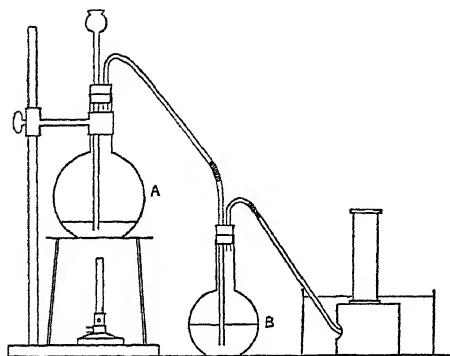


FIG 58

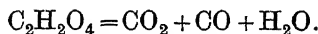
carbon monoxide and dioxide, is passed through a strong solution of sodium hydroxide in flask *B*, to absorb carbon dioxide. The gas is collected over water in a pneumatic trough. Place 20 grams of oxalic acid, $C_2H_2O_4 \cdot 2H_2O$, in flask *A*, and pour in sufficient strong sulphuric acid to cover it. Warm gently and collect a jar or two of the gas.

Test its inflammability and solubility. Fill a soda water bottle under

water $\frac{2}{3}$ with carbon monoxide and $\frac{1}{3}$ with oxygen, and find whether it forms an explosive mixture like hydrogen.

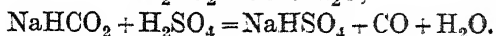
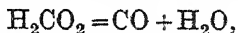
Note that carbon monoxide is a poisonous gas, and carry out all experiments with it in a fume chamber.

The basis of this reaction is the attraction of concentrated sulphuric acid for water or the dehydrating power of sulphuric acid. This effect can be simply shewn by brushing a design on filter paper with dilute sulphuric acid. When the paper is warmed over a Bunsen flame the water evaporates, leaving sulphuric acid which is not volatile at this temperature, and the concentrated acid acts on the paper, turning it black. Paper consists of cellulose, a compound of carbon, hydrogen, and oxygen, which has the formula $(C_6H_{10}O_5)_n$. The $H_{10}O_5$ is removed by the sulphuric acid as $5H_2O$, leaving a residue of black carbon. The equation representing the dehydration of oxalic acid is



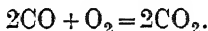
When water is abstracted from oxalic acid, the anhydride C_2O_3 is left which does not exist, but breaks up into CO_2 and CO . The sulphuric acid is not decomposed, so that it is unnecessary to include it in the equation.

Instead of oxalic acid, formic acid, H_2CO_2 , or sodium formate, NaHCO_2 , may be used. In this case the gas is generally pure and does not need treatment with caustic soda.

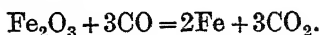


Properties. Carbon monoxide is a colourless gas with a faint smell. It is lighter than air, very slightly soluble in water, and is difficult to liquefy; B.P. -193° . The gas is very poisonous. One volume in 800 volumes of air is sufficient to cause death. Poisoning by coal gas is due to the presence of carbon monoxide, of which it contains about 10%. Combustion or explosion in a confined space such as a mine may result in the production of a poisonous atmosphere, and the exhaust gases from a motor-car also contain carbon monoxide, which may cause discomfort or even danger if a car is ill ventilated or if the engine is kept running in a closed garage. The poisonous properties of carbon monoxide are due to the fact that it forms a compound with the haemoglobin of the blood, changing its colour to bright red. Oxygen is unable to displace carbon monoxide from this compound, so the blood ceases to be oxygenated and death is the result.

Carbon monoxide burns in air with a blue flame, forming carbon dioxide, and gives an explosive mixture with air or oxygen.



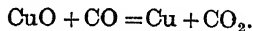
It is a powerful reducing agent, as it has 2 free bonds which readily take up oxygen to form the dioxide. Carbon in the form of coke or coal is used in metallurgical furnaces to extract metals from their ores. These ores are usually oxides or compounds which can be converted into oxides by roasting in air. The ore is mixed with coke or coal and burned in a furnace, giving first carbon dioxide, which is reduced by the glowing carbon to carbon monoxide. In many such cases, for example in iron smelting in the blast furnace, the carbon monoxide is the active reducing agent.



•**Expt.**—To shew that carbon monoxide reduces a metallic oxide. Fit up the apparatus as illustrated. *A* is the generating flask containing oxalic acid and sulphuric acid. *B* is a caustic soda flask to absorb carbon dioxide. *C* is a hard glass tube containing a

little copper oxide. Pass a current of gas through the apparatus till all the air is driven out, using the same precautions as in the case of hydrogen.

Then heat the copper oxide till it is changed into red metallic copper. Remove the flame and allow the copper to cool in a current of the gas. The equation is



Compare this action with the action of hydrogen on copper oxide. How do the products differ?

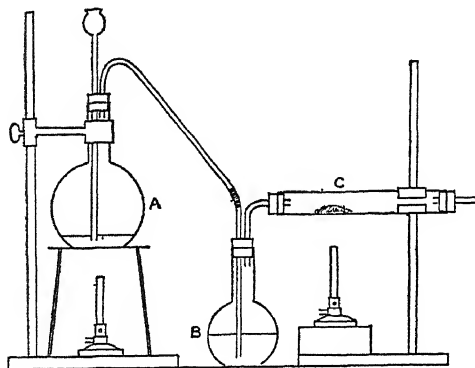
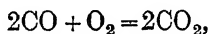


FIG. 59.

Composition. The

composition of car-

bon monoxide may be shown by exploding the gas with oxygen in a eudiometer. Two volumes of carbon monoxide unite with 1 volume of oxygen, giving 2 volumes of carbon dioxide.



2 Vols. 1 Vol. 2 Vols.

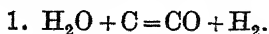
or, 2 molecules of carbon monoxide unite with 1 molecule of oxygen to give 2 molecules of carbon dioxide. Now 2 molecules of carbon dioxide contain 4 atoms of oxygen, 2 of these are supplied by the molecule of oxygen, therefore 2 atoms come from the 2 molecules of carbon monoxide. Consequently the molecule of carbon monoxide contains 1 atom of oxygen, and the formula is C_xO . The vapour density of the gas is 14, and its molecular weight is 28. The atom of oxygen weighs 16, therefore the carbon weighs $28 - 16 = 12$, which is the weight of 1 atom. The formula of carbon monoxide is then CO .

Estimation of Carbon Monoxide. It is absorbed from a mixture of gases by passing through a solution of cuprous chloride in ammonia or hydrochloric acid. The volume absorbed represents the volume of carbon monoxide present.

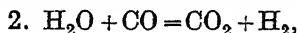
Producer Gas. This is one of a number of important commercial gas mixtures containing carbon monoxide. It is obtained by blowing a stream of air through a bed of white-

hot coke. The composition of the gas is about 35% of carbon monoxide and 65% of nitrogen.

Water Gas. If steam is blown through white-hot coke, water gas is obtained, a mixture of hydrogen, carbon monoxide, and carbon dioxide. When steam interacts with incandescent carbon, hydrogen and carbon monoxide are formed.



At a lower temperature carbon monoxide and steam react together,



giving carbon dioxide and hydrogen. The decomposition of steam takes up so much heat that the producer gradually cools, and unwanted carbon dioxide is produced. The process cannot therefore be continuous. When the furnace cools, it must be blown up to a high temperature with air alone, giving ordinary producer gas. The steam blast is then turned on, the air turned off, and water gas is obtained. The average composition of water gas is:

Hydrogen	-	-	-	-	50%
Carbon monoxide	-	-	-	-	43%
Carbon dioxide	-	-	-	-	3%
Nitrogen	-	-	-	-	4%

Mixed or Dowson Producer Gas. This gas, which is extensively used, is made by blowing a mixture of air and steam

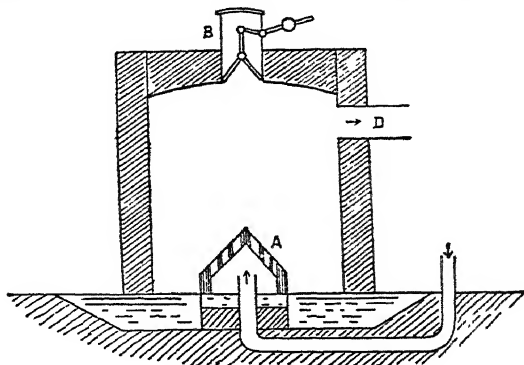


FIG. 60

through incandescent carbon. This process is continuous, as the heat generated by the oxidation of carbon is greater than

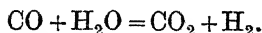
the heat absorbed by the decomposition of steam, so the producer does not tend to cool. The temperature for best working is about 1100° .

The illustration represents a common type of producer. It is a furnace of circular cross-section, made of steel and lined with firebrick, and is about 12 feet high. The fuel, which is usually coal, is supported on a grate *A*, and is admitted through a 'hopper' *B* at the top of the furnace. A cup and cone arrangement prevents the escape of gas when the producer is being charged with coal. The air and steam are blown in below the grate, and the gas passes out through the pipe *D*. The composition of the gas averages:

Carbon monoxide	-	-	25%	Inflammable.
Hydrogen	-	-	18%	
Methane	-	-	1%	
Carbon dioxide	-	-	4%	Non-inflammable.
Nitrogen	-	-	52%	

These gases are used largely in heating furnaces for steel making and for other industrial purposes. The advantages of gas as a fuel over coal are: quick heating, easier regulation of temperature, absence of soot and ash, labour saved in stoking.

Hydrogen is now used in large quantities in the manufacture of synthetic ammonia and the hydrogenation of oils, and can be obtained from water gas by mixing it with steam and passing the mixture over a catalyst such as nickel or oxide of iron, heated to 450° .

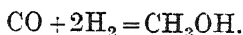


Water gas consists of nearly equal volumes of carbon monoxide and hydrogen. Another volume of hydrogen is obtained from the steam. The hydrogen produced thus contains about $\frac{1}{3}$ of its volume of carbon dioxide, which is got rid of by washing with water and finally with alkalis.

Another method of removing hydrogen from water gas is by compression and cooling. Carbon monoxide is more easily liquefied than hydrogen. Hence if water gas is compressed and cooled sufficiently, the carbon monoxide and dioxide are liquefied while the hydrogen remains in the gaseous state and is stored in cylinders.

Methyl alcohol or wood spirit, CH_3OH , can be made from water gas on a large scale. Water gas mixed with half its

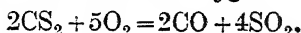
volume of added hydrogen is compressed, heated to 450° , and passed over copper mixed with zinc oxide, which acts as a catalyst.



Methyl alcohol has important uses in the manufacture of dyes, perfumes, varnishes and polishes, and may yet have a future before it, as a substitute for petrol.

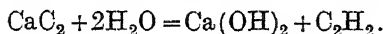
Some Other Compounds of Carbon. Carbon forms compounds with other elements besides oxygen. With hydrogen it gives the **Hydrocarbons**, which will be described in the chapter following.

Carbon Disulphide, CS_2 . This substance is made by passing sulphur vapour over red-hot carbon. The process is generally carried out in an electric furnace. It is a colourless, evil-smelling liquid of high refractive power, and easily vaporised. The vapour takes fire at a very low temperature and forms a violently explosive mixture with oxygen.

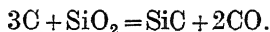


Carbon disulphide dissolves phosphorus, sulphur and rubber.

Carbides. Carbon unites with metals, forming carbides. One of the best known of these is **Calcium Carbide, CaC_2** , which is produced by heating a mixture of lime and coke in an electric furnace. Cold water has a vigorous action on calcium carbide, giving acetylene gas, C_2H_2 , and calcium hydroxide.



Another product of the electric furnace is **Carborundum** or silicon carbide, SiC , made by heating together silica or sand, SiO_2 , and coke.



This substance is exceedingly hard and is used in making grinding and polishing wheels, it belongs to the class of materials known as 'abrasives.'

Additional Experiments

EXPT.—Make carbon monoxide by the action of concentrated sulphuric acid on formic acid. Heat some strong sulphuric acid to about 100° in a flask fitted with dropping funnel and delivery tube. Drop into it concentrated formic acid from the funnel drop by drop, and collect the gas over water. This is an easy method of making the gas.

EXPT.—Pack an iron tube or glass combustion tube with small pieces of charcoal. Heat to bright redness and pass a slow current of air through the tube. Collect the gas over water and test for carbon dioxide and carbon monoxide.

EXPT.—Take a $\frac{1}{2}$ -inch glass tube, 9 inches long. Fill with mercury. Invert it and clamp with the lower end dipping under mercury in a trough. Introduce some carbon monoxide and note level of mercury. Then pass into the tube a few c.c. of ammoniacal cuprous chloride. Note the rise of the mercury.

QUESTIONS

1. How would you prove experimentally that the two oxides of carbon obey the law of multiple proportions ?

(Oxford and Camb. School Cert.).

2. On heating a certain white crystalline substance with concentrated sulphuric acid, a mixture of carbon monoxide and carbon dioxide was evolved. Describe how you would

(a) determine the proportion of each gas,

(b) convert the mixture into carbon monoxide,

(c) convert the mixture into carbon dioxide.

Name a substance that would yield such a mixture of gases, and write the equation for the reaction. (Scot. Leaving Cert.)

3. Describe the preparation and principal properties of carbon monoxide. What is the evidence on which the formula CO is assigned to this gas ? (London Matric.)

4. What chemical change takes place when air is passed through a tube containing red-hot charcoal ? Describe the principal properties of the product. Mention a familiar example of this action. (Scot. Univ. Entrance.)

5. Given a generator supplying carbon dioxide, how would you prepare pure (but not necessarily dry) carbon monoxide ? Describe and sketch the apparatus required. What impurity would you expect in the gas, if precautions were not taken to exclude it ? How would you test for the presence of this impurity ? Give an account of the properties of carbon monoxide. (Scot. Univ. Entrance.)

6. How is water gas prepared ? What are its chief constituents and for what purpose is it used ? How can hydrogen be obtained from it ?

7. Give the name and formula of (a) a compound of carbon and sulphur, and (b) a compound of carbon and calcium. Describe the preparation and the uses of each substance.

CHAPTER XXI

HYDROCARBONS. PETROLEUM. METHANE. ETHYLENE. ACETYLENE. COAL GAS

CARBON atoms have the power, not shared to any extent by the atoms of other elements, of linking together to form chains. In doing so they use one or more of their four bonds, leaving the others free to unite with atoms or groups of atoms of other elements. This chain-forming property enables carbon to take part in the formation of a vast number of compounds, to the study of which a specialized branch of chemistry is devoted, called the **Chemistry of the Carbon Compounds**, or more generally **Organic Chemistry**. A living body, plant or animal, is known as an organism, and the first carbon compounds made were derived from the material of such bodies. Organic compounds are mainly composed of carbon, oxygen and hydrogen, many contain nitrogen, and other elements are frequently present. The first chemical compounds prepared by man were probably alcohol, vinegar or acetic acid, and dyes extracted from plants, all of which are organic substances.

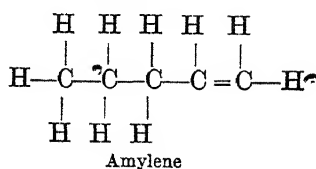
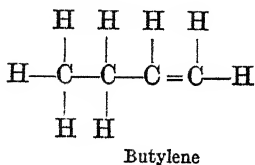
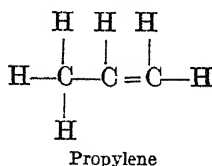
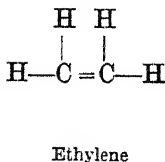
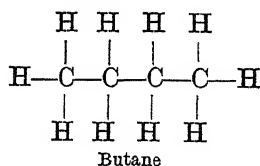
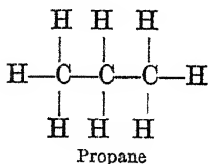
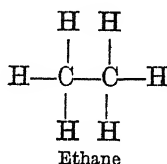
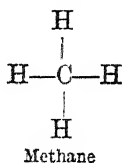
Hydrocarbons. To illustrate the chain-forming power of carbon, let us take the compounds of carbon with hydrogen, the **Hydrocarbons**. We will consider three series of these, the **Paraffin** series, the **Olefine** series, and the **Acetylene** series. Following are the names and formulae of the first three members of each series:

Paraffin Series.		Olefine Series.		Acetylene Series.	
Methane	CH_4	—	—	—	—
Ethane	C_2H_6	Ethylene	C_2H_4	Acetylene	C_2H_2
Propane	C_3H_8	Propylene	C_3H_6	Allylene	C_3H_4
Butane	C_4H_{10}	Butylene	C_4H_8	Crotonylene	C_4H_6

An examination of these formulae shows that in each series consecutive members differ by CH_2 . A series of compounds in

which the molecule increases by steps of CH_2 is called a homologous series. Another point to be observed is that in each case the number of hydrogen atoms has a definite arithmetical relationship to the number of carbon atoms. In the paraffin series the number of hydrogen atoms is equal to twice the number of carbon atoms plus two, and the general formula may be written algebraically as $\text{C}_N\text{H}_{2N+2}$. In the olefine series again, the number of hydrogen atoms is exactly double the number of carbon atoms, and the formula is C_NH_{2N} . In the acetylene series the general formula is $\text{C}_N\text{H}_{2N-2}$. We can thus write the chemical formula of any hydrocarbon if we know the number of carbon atoms which it contains and the series to which it belongs.

Graphic formulae give a clearer picture of the constitution of these compounds.



In every case, the formula of the next higher member of a series is derived by replacing a hydrogen atom at the end of the chain by CH_3 , which is equivalent to an addition of CH_2 .

The Paraffin Series. The paraffins are so named because they are found in petroleum or paraffin oil. Petroleum is a thick greenish oil found in large quantities in the United States of America, in Russia, Persia, and other countries. Oil is obtained by boring, and is frequently confined under such high pressure that when the bore is sunk and the miner 'strikes oil' it shoots out with such violence that a 'gusher' or fountain perhaps 100 feet in height is formed, which may last for hours or even days.

Petroleum is separated by distillation into 'fractions.' The following are some of the products obtained, with their boiling points.

Petrol	-	-	-	-	-	50°-150°
Paraffin oil	-	-	-	-	-	150°-300°
Lubricating oil and vaseline	-	-	-	-	-	300°
Paraffin wax	-	-	-	-	-	Solid, M.P. 45°-65°

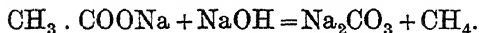
The first four members of the paraffin series are gases. From C_5H_{12} to $\text{C}_{15}\text{H}_{32}$ they are liquids, and above this they are solids.

Methane, CH_4 . This is the first of the paraffins.

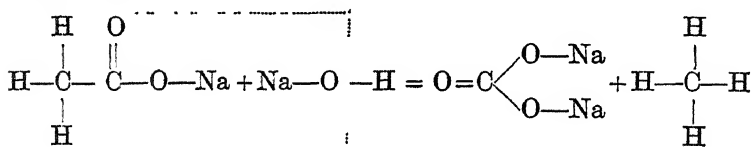
Occurrence. It is obtained from wells in large quantity in the U.S.A., and is known as 'natural gas.' It is also called Marsh Gas because it is produced by the decay of vegetable matter in marshy places. When a stagnant pool is stirred up bubbles of marsh gas may sometimes be noticed rising to the surface. In coal mines methane is often present in a highly compressed state in the coal, from which it may be accidentally released by mining operations or even by a sudden fall of atmospheric pressure. The gas, called by miners 'fire damp,' is inflammable and forms an explosive mixture with air, so that its presence in a mine is a frequent cause of violent explosions. To guard against these, coal miners are not permitted to use naked lights, but are provided with 'safety lamps,' the principle of which will be explained later. The atmosphere in a coal mine may contain besides oxygen and nitrogen, methane, carbon monoxide and carbon dioxide, and various mixtures of these gases are known by the general term 'damp' (the miners' word for a gas). Some of these are 'fire damp,' 'black damp,' 'white damp,' 'after damp.'

Preparation

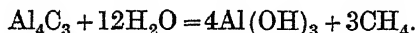
1. Methane is usually prepared in the laboratory by heating a mixture of dried or fused sodium acetate with 3 times its weight of soda lime. Soda lime is made by slaking quicklime with strong caustic soda solution and heating till dry. As strong heating is required, the mixture of sodium acetate and soda lime should be contained in a flask of copper or hard glass. The gas is collected over water. Methane prepared in this way is not quite pure, it usually contains hydrogen,



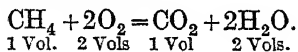
The reaction becomes clearer when the formulae are written graphically,



2. The action of water in the cold on aluminium carbide gives methane, which may contain a little acetylene.



Properties. Methane is a colourless gas, without taste or smell. It burns with a pale blue flame and forms a violently explosive mixture with oxygen.



One volume of methane requires two volumes of oxygen and consequently ten volumes of air to give the most explosive mixture. It does not support combustion, as may be shewn by dipping a burning taper into a jar of the gas. The formula

$\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{H} \end{array}$

of methane, $\text{H}-\text{C}-\text{H}$, shews that all the carbon bonds are

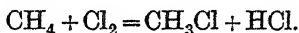
engaged; it is therefore a 'saturated' compound, unlike carbon monoxide, $=\text{C}=\text{O}$, which has two free bonds, so no more atoms can be added to the methane molecule.

Substitution Compounds. However, the hydrogen atoms can be replaced by other atoms or groups of atoms. For example, chlorine atoms can be substituted and four compounds known as **Substitution Compounds** are obtained.

CH_3Cl	mono-chloromethane or methyl chloride,
CH_2Cl_2	di-chloromethane or methylene chloride
CHCl_3	tri-chloromethane or chloroform,
CCl_4	tetra-chloromethane or carbon tetrachloride.

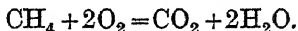
These compounds may be formed by the direct action of chlorine on methane, the hydrogen in each case going to form hydrochloric acid, but they are usually prepared by indirect methods.

Chloroform or tri-chloromethane is largely used as an anaesthetic and as a solvent.



Carbon Tetrachloride is also a good solvent for grease, tar, and other organic substances, and is employed in the process of dry cleaning.

Composition. This is determined by exploding a known volume of methane with excess of oxygen in a eudiometer.



The carbon dioxide is absorbed by caustic soda, and the remaining gas is the excess of oxygen. The volume of oxygen taking part in the reaction and the volume of carbon dioxide produced can thus be ascertained. It is found that 1 volume of methane unites with 2 volumes of oxygen, giving 1 volume of carbon dioxide ;

\therefore 1 molecule of methane gives 1 molecule of carbon dioxide, but 1 molecule of carbon dioxide contains 1 atom of carbon ;

\therefore 1 molecule of methane contains 1 atom of carbon, and the formula is CH_x .

Again, 1 volume of oxygen has united with carbon to form 1 volume of CO_2 , but 2 volumes of oxygen take part in the reaction ;

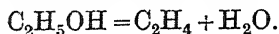
\therefore 1 volume of oxygen has united with hydrogen to form water,

and 1 molecule or 2 atoms has formed 2 molecules of water, $2\text{H}_2\text{O}$.

Now 2 molecules of water contain 4 atoms of hydrogen,
 \therefore 1 molecule of methane contains 4 atoms of hydrogen,
 and its formula is CH_4 .

Ethylene, Olefiant gas, C_2H_4 , is the first member of the Olefine series.

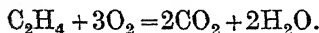
Preparation. 1. It is generally prepared by the dehydrating action of concentrated sulphuric acid on alcohol, $\text{C}_2\text{H}_5\text{OH}$.



Make a mixture of 50 c.c. of alcohol and 150 c.c. of strong sulphuric acid. Heat it in a 2-litre flask fitted with a dropping funnel and delivery tube. The gas is passed through strong caustic soda to absorb any sulphur dioxide formed, and collected over water. The materials in the flask may be renewed by adding through the funnel a mixture of equal parts of alcohol and sulphuric acid. Have bulb on delivery tube to prevent caustic soda sucking back.

2. Probably a better method is to use syrupy phosphoric acid as the dehydrating agent. Place 50 c.c. of the acid in a flask, heat it up to 200° and add alcohol drop by drop from the dropping funnel. Frothing is avoided, which may be troublesome in the first method.

Properties. Ethylene is a colourless gas with a sweet taste and pleasant smell. It is slightly soluble in water. It burns in air with a luminous smoky flame and forms an explosive mixture with oxygen.



1 vol 3 vols. 2 vols

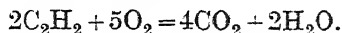
One volume to three volumes is the proportion for the most explosive mixture.

Acetylene is the first member of the acetylene series.

Preparation. Acetylene is made by the action of water on calcium carbide. A little carbide is placed in a flask with tap-funnel and delivery tube. Water is admitted drop by drop, and the gas collected over water.

Properties. Acetylene is a colourless gas. When perfectly pure it has a pleasant smell, but as ordinarily prepared it contains impurities which give it a disagreeable odour. When a Bunsen burner 'strikes back' and burns at the lower jet with an insufficient supply of air it gives off a smell which is

generally associated with the acetylene which is formed, but is probably due to some other substance. Acetylene burns in air with a luminous smoky flame, but burned with a specially made jet the flame is brilliantly white and smokeless. When mixed with oxygen in the proper proportions and fired, it explodes with extreme violence.



Acetylene is very unstable and may be exploded by pressure, so that it cannot be compressed, like other gases, into steel cylinders with safety. The gas is passed into acetone, which absorbs 300 times its own volume at a moderate pressure, and the solution is transferred to cylinders filled with some absorbent material which soaks up the liquid.

Uses. The union of carbon and hydrogen to form acetylene is an 'endothermic' reaction and is accompanied by a considerable absorption of heat. When such a substance is decomposed, the heat absorbed in its formation is given out, so that when acetylene is burned in oxygen this heat is obtained in addition to the heat developed by the burning of hydrogen and carbon, and the temperature of the flame is the highest obtainable from any gas with the exception of atomic hydrogen. The oxy-acetylene flame produced by the oxy-acetylene blow-pipe is said to have a temperature of about 4000° , and is much used for welding and cutting metals. The flame will cut through a 6-inch bar of steel in less than one minute.

Acetylene is used occasionally for illuminating purposes in country houses where neither coal gas nor electricity is available, and is commonly employed for bicycle lamps.

Coal Gas

History. In 1688 the Rev. John Clayton prepared coal gas by distilling coal, and carried out some experiments with it. It remained more or less a scientific curiosity until 1792, when William Murdoch, who may be regarded as the pioneer of gas-lighting, used it for the illumination of his house in Cornwall. Within the next twelve years he had installed gas-lighting in several factories in Birmingham and Manchester, and in 1812 the new illuminant was adopted in London, Paris following suit shortly after. From this time on its use spread rapidly.

Manufacture of Coal Gas. In gas-works bituminous coal is heated in fireclay retorts. These may be horizontal, but in

most modern plants are vertical, a type which, among other advantages, makes stoking much less laborious.

The gas passes from the retorts, *A*, to the 'hydraulic main,' *B*, containing water, which retains much of the ammonia and tar and acts as a 'water seal,' preventing gas passing back into the retort when it is opened. From the hydraulic

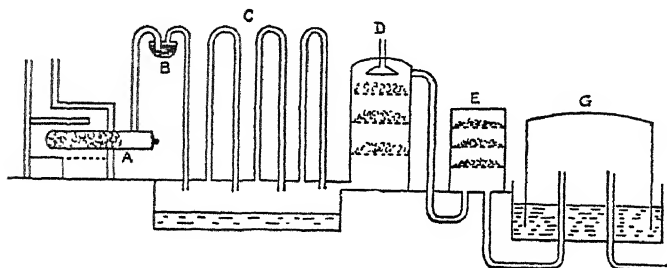


FIG. 61.

main the gas enters the 'condensers,' *C*, where more tar and ammonia are absorbed. It then goes to the 'scrubbers,' *D*, iron towers packed with coke kept wet by a stream of water, and is freed from the last traces of tar and ammonia. The gas still contains hydrogen sulphide (sulphuretted hydrogen), carbon disulphide and some carbon dioxide. These impurities are removed in the 'purifiers,' *E*, which contain trays covered with 'bog iron ore' (a hydrated oxide of iron), or lime. The purified gas finally enters the 'gas-holder' or 'gasometer,' *G*, an iron bell sealed below with water.

Composition. An average composition of coal gas from vertical retorts is:

Hydrogen	-	-	-	-	50%	Heat-giving but non-illuminating.
Methane	-	-	-	-	18%	
Carbon monoxide	-	-	-	-	19%	
Ethylene, acetylene and benzene	-	-	-	-	3%	Illuminating.
Nitrogen	-	-	-	-	6%	Impurities.
Carbon dioxide	-	-	-	-	4%	

The illuminating power of coal gas is entirely due to the ethylene, acetylene and benzene which it contains. When these are removed, or destroyed by distillation at a high temperature, the gas loses its luminosity or light-giving power. To restore this, gas mantles are used. They consist of cones

made of cotton soaked in thorium nitrate, dried, and dipped in collodion to harden them. When they are put in place on the gas burner and 'burnt off,' a skeleton of thorium oxide remains which becomes white hot in the gas flame and gives a brilliant light.

Products of Gas Making

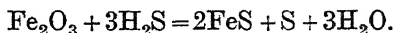
1. Coal Gas. A ton of good coal should produce about 11,000 cubic feet of gas.

2. Coke. The residue left in the retort after distillation is coke. It is removed red hot and quenched with water. The weight of coke contained is 65-70% of the weight of coal distilled; it is known as gas coke and is used as a fuel. Coke is difficult to light and slow burning, but gives out great heat.

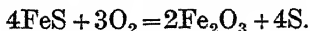
3. Tar. About 11 gallons of tar are recovered from a ton of coal. It is a very complex mixture of compounds and a valuable by-product, from which various oils are distilled, leaving a residue of pitch. A few of the innumerable substances derivable from coal tar have already been mentioned.

4. Ammonium Sulphate. Coal contains about 1% of nitrogen, part of which is given off as ammonia, NH_3 , in distillation. This is absorbed in the condensers and scrubbers, giving 'ammoniacal liquor' containing ammonium hydroxide and salts of ammonium. The liquor is heated with steam and milk of lime, and the ammonia gas evolved is absorbed in sulphuric acid, with which it combines to form ammonium sulphate. The average yield per ton of coal is 20-25 pounds.

5. Sulphur. When the oxide of iron in the purifiers is mainly transformed into sulphide by the hydrogen sulphide gas, it ceases to be effective as an absorber and is then known as 'spent oxide.'



It is then removed and exposed to the air, which oxidizes it back to the oxide again, setting free sulphur.



The oxide can thus be used over and over again. The quantity of free sulphur, however, increases each time until it reaches about 50%, when the oxide is no longer useful as a purifier. Still its usefulness is not at an end, as its large content of sulphur makes it a suitable material for the manufacture of sulphuric acid.

Additional Experiments

EXPT.—Explode a mixture of two-thirds oxygen and one-third methane in a soda-water bottle.

EXPT.—Reduce copper oxide with methane in a combustion tube. Note formation of water and carbon dioxide.

EXPT.—To show action of bromine on ethylene. Introduce into a flask of ethylene a small thin glass bulb containing a little bromine. Cork flask and shake to break the bulb. Open flask under water and note inrush of water.

EXPT.—Make some acetylene by dropping water on calcium carbide, collect a cylinder and test with a flame.

QUESTIONS

1. Describe methods by which methane and ethane are produced. Write a short account of the paraffin series.

2. Starting from acetic acid, give an exact account of what you would do to obtain several jars of methane. What experiments would you perform in order to show the chief properties of the gas ?
(London Matric.)

3. What is the effect of intensely heating together lime and carbon ? What compound of carbon and hydrogen is formed when the product is treated with water ? Mention some other common compound of hydrogen and carbon which burns in air with a luminous flame, state how it is prepared and compare its properties with those of the former compound.

(London Matric.)

4. Calculate what volume of oxygen measured at 13° C. and 741 mm. pressure is required for the complete combustion of the methane which may be obtained from 4.1 grams of anhydrous sodium acetate.

(London Matric.)

5. How would you prepare and collect a quantity of carbon monoxide ? Contrast its chief properties with those of carbon dioxide. Hydrogen, marsh gas, and carbon monoxide all burn with blue flames. If one of these gases were burning at a jet, what experiments would you make to ascertain which gas it was ?

6. Describe the manufacture of coal gas. Mention four important by-products, and give some account of the uses to which they are put.

(Scot. Leaving Cert.)

CHAPTER XXII

COMBUSTION. IGNITION TEMPERATURE. DAVY LAMP. LUMINOSITY

Combustion. The commonest form of combustion, with which we are all familiar, is the burning of substances in air, the process known as oxidation. However, all combustions are not oxidations; for example, hydrogen and antimony burn in chlorine.

The outward evidences of combustion are light and heat, so the term may be defined as 'a chemical reaction which is accompanied by evolution of heat and production of light.'

We say that a gas which burns is 'combustible,' and that the atmosphere in which it burns is a 'supporter of combustion.' According to this coal gas is combustible and our atmosphere is a supporter of combustion. But these terms are really reversible, for we can burn air in coal gas just as easily as coal gas in air.

EXPT.—Take an ordinary lamp chimney and fit the bottom with a cork pierced with two holes to admit two glass tubes, as in the illustration. Tube *A*, which should be about $\frac{1}{2}$ -inch diameter, is intended for admission of air. Tube *B*, about $\frac{1}{4}$ -inch, is attached by rubber tubing to a gas tap. Cover the top of the chimney with a piece of sheet asbestos having a circular hole $\frac{1}{2}$ -inch in diameter. First lay a sheet of paper on the asbestos to cover up the hole loosely. Then turn on the gas to fill the chimney, and after a minute or so, by which time all the air should be expelled, light the gas at the tube *A* and at the same moment remove the sheet of paper. The flame will ascend to *C*, where air burns in coal gas, and the gas will also ignite at *D*, where coal gas burns in air.

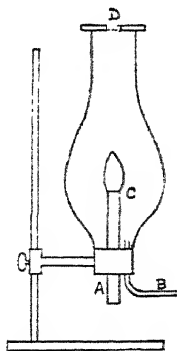


FIG. 62.

If our atmosphere consisted of coal gas and if our bodies were so constructed that we could live in it, we should have to burn air or oxygen at our gas jets.

In the same way it can be shown that hydrogen burns in chlorine and chlorine in hydrogen, so that gases which we ordinarily call 'supporters of combustion' may under other conditions be combustible.

Flame was regarded by the early philosophers as one of the four elements, and many speculations were made with regard to its nature. The first important attempt to explain combustion was made by John Mayow in 1674, who conducted an ingenious series of experiments and made deductions from them which were remarkably near the truth as we now know it. He considered that combustion and breathing were analogous processes, and that air contained particles which were necessary for both, but the erroneous phlogiston theory so dominated chemical science that his work was neglected and forgotten for 100 years till the experiments of Lavoisier, Priestley and Cavendish proved that combustion in air is an oxidizing action.

Ignition Temperature. We are already familiar with the fact that the application of heat is often required to start a chemical reaction. A cold jet of hydrogen or coal gas shows no sign of combustion when it meets the air. It has to be heated up to its **Ignition Temperature**, and it is sufficient that a very small quantity of the gas be heated, *e.g.* by a spark. Combustion takes place at that point and rapidly spreads through the whole mass of gas, but the heat given out by the reaction must be sufficient to raise the adjoining molecules to their ignition temperature. When air is sparked, combination of nitrogen and oxygen takes place, and oxides of nitrogen are formed. Heat is not given out but absorbed in the reaction, so that the adjacent molecules are not heated up to ignition point and combustion does not spread. Were it otherwise, a flash of lightning might cause the combustion of all the oxygen in the world's atmosphere.

Expt.—1. Hold a sheet of wire gauze an inch or two above a Bunsen burner and turn on the gas. Light the gas above the gauze and observe that it does not take fire below till the iron becomes red hot.

2. Press the sheet of gauze down on a gas flame, in this case the gas does not light above the wire till it gets red hot.

In the first experiment, the heat is conducted away so rapidly that the temperature of the iron does not rise for some time to the ignition temperature of coal gas, and thus the flame does not spread below. In the second case for the same reason the gas does not light above the gauze till the iron has reached the ignition temperature.

The Davy Lamp. Considerations such as these suggested to Sir Humphry Davy, in 1815, the idea of the miner's safety lamp. Before that time fire-damp explosions were of frequent occurrence in 'fiery' coal pits, and the use of the Davy lamp reduced the number of these disasters very considerably. In its original form it consisted of an oil lamp surrounded by a cylinder of fine iron wire gauze, 6 inches high and $1\frac{1}{2}$ inches in diameter, and closed in at the top with the same material. The original lamp gave a very feeble light, but the modern improved type, in which the lower part of the cylinder is glass, gives a far better illumination and can be used safely in very explosive atmospheres. In such conditions the fire-damp passes through the gauze and burns inside the lamp; there is no danger of an explosion unless the gauze is heated up accidentally to the ignition temperature of the surrounding gas mixture.

The ignition temperature of burning oils such as petroleum is important, as oils with too low an ignition temperature, or 'flash point,' might give dangerous explosions. The flash point of lamp oil must not be below 73° Fahrenheit.

Each inflammable substance has its own ignition temperature.

EXPTS.—1. In a test tube dissolve a small piece of yellow phosphorus in a very little carbon disulphide, *do not heat*. Pour a few drops of the solution on a piece of filter paper and spread it out to dry. When the carbon disulphide has evaporated the phosphorus takes fire.

2. Place a small piece of phosphorus in a basin and touch it with a glass rod slightly warmed in the flame.

3. Pour a few drops of carbon disulphide into a basin and hold in the vapour a glass rod heated a little more strongly.

4. Repeat the last experiment with ether, benzene and alcohol. ~~test~~ testing with a glass rod and a burning taper.

The finely divided phosphorus left after the evaporation of carbon disulphide ignites spontaneously at room temperature.

A warm glass rod will ignite a piece of phosphorus, but requires to be a little hotter to ignite carbon disulphide. Ether requires a red-hot rod, and benzene and alcohol a lighted taper.

Luminosity of Flame. Flames may be luminous or non-luminous. The flame of a candle is typical of the first class,



FIG. 68 —
Candle Flame.

the hydrogen or Bunsen flame of the second. A candle flame consists of 4 parts, (1) the dark inner cone of unburnt gas round the wick, (2) the yellow luminous region which gives all the light, (3) a small bright blue cup at the base, and (4) a faintly luminous mantle which entirely surrounds the flame. The luminous part is called the zone of incomplete combustion, and contains small particles of carbon in a state of incandescence which will deposit as soot on a cold surface. The outer non-luminous mantle is called the zone of complete combustion, where the carbon particles are oxidized to carbon dioxide and the hydrogen to water. Liquids and solids must be converted into vapour before they can burn with a flame, and the wick of a candle assists this change. The wax, which consists of hydrocarbons, is melted and drawn up into the wick by capillary attraction. It is then converted into vapour by the heat of the surrounding flame, is decomposed into hydrogen, and carbon particles which become incandescent, and is finally completely oxidized in the outer mantle.

A candle flame, then, is luminous because it contains solid particles of glowing carbon. The constituents of coal gas which give luminosity to the flame of an ordinary burner are the hydrocarbons, ethylene, acetylene and benzene, and these decompose in the same way as in the candle flame.

Luminosity is not always due to the presence of solid particles, as it can be proved that in some luminous flames no solid particles exist. There is no universal explanation of the phenomenon, but it is established that flame can be rendered more luminous by increase of pressure and rise of temperature.

The Bunsen Burner. In the Bunsen burner coal gas is mixed with air to give more perfect combustion, a hotter flame, and freedom from smoke or soot. The gas and air are admitted through openings at the base and mix in the tube. It will be noticed that when air is admitted to the flame by turning the collar on the burner, the flame diminishes in size. The amount

of gas consumed is the same and the heat produced by chemical combination is therefore the same, so as the flame is smaller it must necessarily be hotter. As more and more air is admitted the flame becomes smaller and smaller, until finally the admission of any more causes the flame to descend to the bottom of the tube. This takes place when the gas and air are in the proportions of an explosive mixture, and the speed of the flame travelling in the mixture is greater than the speed at which the mixture passes up through the burner. At this point the flame jumps down the tube or 'strikes back.'

The flame of a Bunsen burner with the air holes open is non-luminous. It consists of 3 parts, (1) the inner cone of unburnt gas, (2) a blue cone, the zone of incomplete combustion, and (3) a pale blue outer cone, the zone of complete combustion.

EXPT.—To show the different zones of a candle or Bunsen flame, depress upon it for a few seconds a piece of cardboard, a piece of asbestos paper or a piece of copper foil.

EXPT.—To show the presence of unburnt gas in the inner zone, insert into it one end of a 6-inch narrow glass tube; the gas can be ignited at the other end. A pin pushed through a match about $\frac{1}{2}$ -inch from the head may be laid across the top of a Bunsen, with the match head upwards. If the gas is then lighted, the match remains in the centre of the flame without igniting.

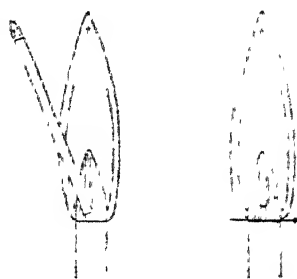


FIG 64

Additional Experiments

EXPT.—Rub a piece of stiff white paper over with a coating of mercuric iodide. Press down on the Bunsen flame and remove before it scorches. Observe the red centre and yellow ring. Mercuric iodide when heated turns yellow.

EXPT.—Show the mantles in a gas flame by means of Smithell's 'flame separator.' This consists of an inner and an outer glass tube. The inner has a cork at its lower end by which it can be fixed on to a Bunsen burner. The outer tube is wider and shorter. It also carries at its lower end a rubber stopper with a hole fitting the inner tube, so that it can be slid up and down easily. The inner tube is attached to the burner, and the outer tube is slid down

until the tops of both tubes are at the same level. The gas is then turned on with the air holes open and lighted at the top of the tubes. Air is admitted to the Bunsen till the flame is non-luminous. Then the outer tube is pushed up; and the outer cone of the flame moves up with it while the inner cone burns at the top of the inner tube. The quantity of air admitted to the Bunsen has to be adjusted until a successful result is obtained. By reducing the supply of gas gradually the effect known as *striking back* can be observed.



FIG 65—Smithell's
Flame Separator

EXPT.—Pass the gas from a Bunsen burner with the air holes open into a U-tube, one limb of which contains a plug of cotton wool wetted with benzene. Each limb of the tube is furnished with a jet of metal or pipeclay. When the gas is lighted, the jet containing benzene vapour gives a luminous flame.

EXPT.—Hold the luminous flame of a fishtail burner against an iron plate. There is a decrease of luminosity due to cooling of the flame. If the plate is heated on the opposite side by a blast burner the luminosity is restored.

EXPT.—Make a tube of sheet copper, 9 inches long, to fit over the top of a Bunsen burner. Clamp the burner in a sloping position and light the gas at the end of the extension, using the non-luminous flame. Heat the copper tube midway with another burner, the flame gains luminosity.

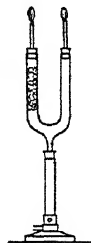


FIG 66

QUESTIONS

1. Compare and contrast present-day views with those held in the eighteenth century regarding the nature of combustion.
(Scot. Leaving Cert.)
2. What two processes of combustion go on in a Bunsen flame? How can they be separated and recognised? (London Matric.)
3. How has the origin of the luminosity of a coal gas flame been investigated? In what ways can the luminosity of such a flame be increased or diminished? Explain how the change is brought about in each case.
(London Matric.)
4. What is meant by the term combustion? Give two instances of combustion in which oxygen does not take part. 'Combustible substance' and 'supporter of combustion' are interchangeable terms. Illustrate this by describing in detail two experiments in

which the 'combustible' in one case becomes the 'combustion supporter' in the other. (Scot. Univ. Entrance.)

5. What is meant by the 'ignition temperature' of substances? Describe some experiments illustrating your answer.

6. A gaseous mixture contains (by volume) 30% of carbon monoxide, 50% of hydrogen, and 20% of incombustible gas. What is the minimum volume of air which must be added to 100 c.c. of the mixture so that, on ignition, complete combustion may take place? Air may be regarded as containing 20% of oxygen by volume.

CHAPTER XXIII

NITROGEN AND AMMONIA

THE discovery of nitrogen is generally ascribed to Prof. Rutherford of Edinburgh University (1772). John Mayow had a century before concluded that air consists of two gases. He shewed that after burning a candle in a globe of air over water the volume of the air decreases, and the gas which is left does not support combustion. Rutherford, proceeding on the same lines, removed oxygen from air by burning in it charcoal and phosphorus, and also separated the products of combustion by means of alkalies and lime water. The residual gas he called, in accordance with the current theory of his time, 'phlogisticated air.' He made experiments showing that it cannot support combustion or respiration. These experiments were afterwards confirmed by H. Cavendish (1784), who also showed that 'phlogisticated air' is a constituent of nitre or saltpetre and nitric acid. Lavoisier gave it the name 'azote,' indicating that it does not support life. In 1823 the present name **Nitrogen**, meaning 'nitre producer' or 'nitre generator,' was proposed by J. A. Chaptal.

Occurrence. Nitrogen forms nearly $\frac{4}{5}$ of the volume of atmospheric air. It is found in nature in combination as potassium nitrate or saltpetre and sodium nitrate or Chile saltpetre. It is also found in soils in salts of ammonium, and is an important constituent of the tissues of plants and animals.

Preparation. 1. We have already seen that nitrogen can be prepared by burning phosphorus in a bell jar of air over water.

2. Nitrogen can be obtained by passing air through a tube containing red-hot copper, which combines with the oxygen, forming cupric oxide.

EXPT.—The air may be supplied by a gas-holder or displaced from a bottle *A* by means of water. It is passed through a solu-

tion of sodium hydroxide to remove carbon dioxide, and then through a tube *C*, containing as long a layer as possible of copper turnings heated red hot by a suitable burner or row of burners.

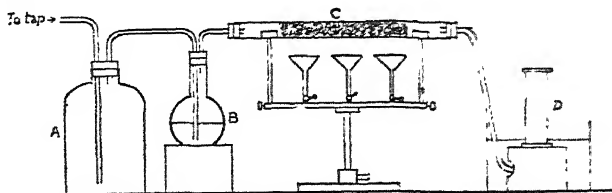
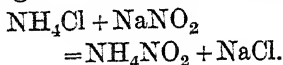


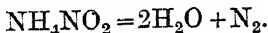
FIG. 67

The absorption of oxygen is rather slow, so the admission of air must be carefully regulated; the flask *B* helps with this. The nitrogen is collected over water in the gas jar *D*.

3. The nitrogen obtained by these methods from air is not perfectly pure as it contains about 1% of argon and the other inert gases. To make chemically pure nitrogen, heat ammonium nitrite. This is the easiest laboratory method of making nitrogen. As ammonium nitrite, NH_4NO_2 , is rather unstable, a mixture of ammonium chloride and sodium nitrite in solution is generally used. We may suppose that the reaction takes place in two stages. On mixing in solution,



On heating,



EXPT.—Fit up a flask with cork and delivery tube, and clamp it on a retort stand. Mix about 10 grams of ammonium chloride and 10 grams of sodium nitrite, place in the flask and dissolve in 50 c.c. of water.

Heat gently with the Bunsen flame, keeping a basin of water ready to cool the flask if the action becomes too violent, and collect over water. Test the gas with a lighted taper.

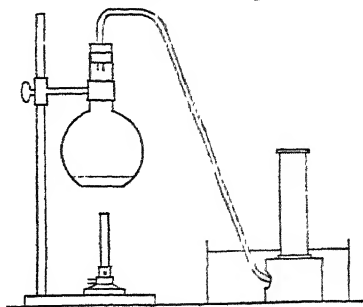
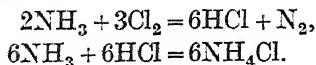


FIG. 68.

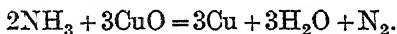
Note particularly that in this experiment ammonium *nitrite* is used, not ammonium nitrate, which gives an oxide of nitrogen on heating.

4. Nitrogen can also be made by passing a stream of chlorine through strong ammonia solution. The chlorine takes hydrogen from the ammonia to form hydrochloric acid, which unites with more ammonia, giving ammonium chloride, and nitrogen is set free.



The ammonia must be in excess or there is a danger of forming the violently explosive nitrogen chloride, NCl_3 , a yellow oily liquid. This substance cost its discoverer, Dulong, the loss of three fingers and one eye, yet this did not deter him from continuing to investigate its properties.

5. Another method of obtaining nitrogen is by passing ammonia gas over heated copper oxide. The ammonia is obtained by heating in a flask some strong ammonia solution, and is passed over copper oxide heated in a tube, and collected over water.



6. Commercially, nitrogen is made by the fractional distillation of liquid air. As it is more volatile than oxygen, it boils off first from the liquid mixture and is collected and compressed into iron cylinders.

Properties. Nitrogen is a gas, colourless, odourless and tasteless. It will neither burn nor support combustion. Though not poisonous, animals die in it, as they die in any gas which does not provide oxygen. At 0°C . 100 volumes of water dissolve 2.4 volumes of nitrogen. By pressure and cooling it can be condensed to a colourless liquid boiling at -194° and frozen to a white solid melting at -214° . Nitrogen gas is chemically very inert, possibly due to the strong mutual attraction of the atoms in its molecule N_2 . But many of its compounds, where we have to do with atomic nitrogen, show great activity. It is an important constituent of many powerful explosives, for example, nitroglycerine, tri-nitro-toluene and picric acid. Nitrogen chloride, NCl_3 , is one of the most violently explosive substances known.

Compounds. The atom of nitrogen may have a valence of 3 as in ammonia, NH_3 , or 5 as in nitrogen pentoxide, N_2O_5 . Just as metals unite with oxygen to form Oxides, so a few when heated in nitrogen combine with it forming Nitrides. Examples of these are aluminium nitride, AlN , and magnesium nitride,

Mg_3N_2 . The formation of the latter can be shewn by the following experiment.

EXPT.—Take a hard glass tube, drawn out at one end and fitted with a one-hole rubber stopper. To the narrow end attach a piece of rubber tubing carrying a clip. Through the stopper pass a bent glass bulb tube, its lower end dipping into a beaker containing coloured water. Place some powdered magnesium in the hard glass tube. Remove the clip and pass a current of nitrogen through the tube till all air has been expelled, then replace clip. Heat the magnesium strongly with a good burner. Heat expansion will cause the nitrogen to bubble through the water, but after a time this will cease and the water will rise in the tube, shewing that the gas is being absorbed by the magnesium.

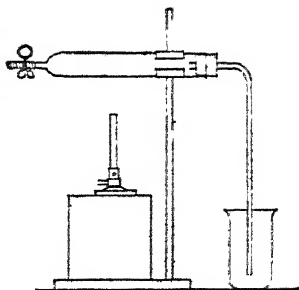
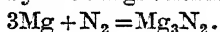
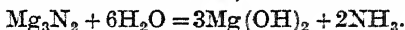


FIG. 69.



The object of the bulb is to prevent the tube being cracked by water sucked back. When the magnesium is cool, remove it from the tube, moisten it with hot water, and note the smell of ammonia.



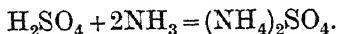
This is a general action of water on nitrides. Nitrides are also prepared by heating metals in ammonia gas.

Ammonia, NH_3 . Ammonia is produced when organic matter, horns, hoofs, bone, is strongly heated, hence the old name for ammonia solution is 'spirits of hartshorn.' Its compound with hydrochloric acid, ammonium chloride, was known to Geber and the Egyptian chemists. This was originally called 'sal armoniacum' or 'salt of Armenia,' but as this name was also applied to common salt and natural sodium carbonate, it was afterwards changed into 'sal ammoniac,' a name which it still retains. The Rev. Stephen Hales (1727), who along with John Mayow was one of the originators of the methods of collecting gases over water, made ammonia gas by heating sal ammoniac with lime in a retort, and tried to collect it in this way. He found, however, that no gas appeared, indeed the water was sucked back into the retort. We know now, of course, that the reason that ammonia cannot be collected over water is its extreme solubility. In 1774, Priestley succeeded in collecting the gas over mercury and called it 'alkaline air.'

Occurrence. Ammonia is given off during the decay of animal matter containing nitrogen. Ammonium sulphate is found in the fumaroles or steam springs of Tuscany.

Preparation

1. The most convenient laboratory method of obtaining ammonia is by boiling strong ammonia solution in a flask. The gas is dried by passing it through a cylinder containing lumps of quicklime. Sulphuric acid, which is commonly used for drying gases, absorbs ammonia, forming ammonium sulphate,



and calcium chloride forms a compound with ammonia, hence the use of these two drying agents is prohibited. As already said, the gas cannot be collected over water, but may be collected over mercury. As

the density of ammonia, 8.5, is only about half that of air, it can also be conveniently collected by upward displacement of air.

2. Ammonia is generally made by the original method used by its discoverers.

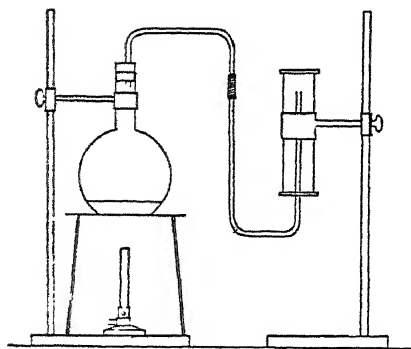


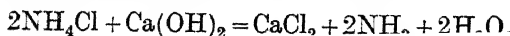
FIG 70.

EXPT.—Mix some ammonium chloride and some slaked lime with a little water in a flask and heat. If required the gas may be dried as already explained.

Collect two or three cylinders of it by upward displacement, and apply the following tests.

1. Note its characteristic smell.
2. Test its effect upon moist litmus paper.
3. Moisten the end of a glass rod with strong hydrochloric acid and hold it in the gas. Observe the white fumes of ammonium chloride.

The equation representing the reaction is :



Commercial Method. Ammonia is obtained as a by-product in the manufacture of coal gas. Coal contains small quantities of nitrogen and hydrogen, which form ammonia when the coal is heated in retorts. The ammonia is absorbed in water and the solution boiled with lime; the expelled ammonia is passed into sulphuric acid, obtaining ammonium sulphate (p. 165).

Fixation of Atmospheric Nitrogen. There are several modern processes by which the nitrogen in the atmosphere is converted into ammonia; to these is applied the general term 'fixation of atmospheric nitrogen.'

This is one of the most important discoveries of chemistry in modern times, and for the following reasons. We have seen that combined nitrogen is an indispensable constituent of all plants and animals. Animal life is ultimately dependent on plant life. There is abundance of nitrogen in the air, but very little of this is assimilated by plants. Most obtain their nitrogen from nitrates and other nitrogen compounds in the soil, but some, such as beans, peas and clover, known as leguminous plants, are able to convert the nitrogen of the air into nitrate and nitrite, which they use as food. This process is carried out by certain 'nitrifying' bacteria which attach themselves to the plant roots and establish chemical factories, one class of workers busying themselves in making nitrate, another in producing nitrite. Oxides of nitrogen are formed in the atmosphere by electrical discharges and washed into the soil, giving nitric acid and nitrates. The decay of organic matter containing nitrogen results in the addition of ammonium salts to the soil. There is thus a continuous circulation of nitrogen in nature. Animals consume food containing nitrogen, then give it back, partly as nitrogen partly as ammonia, to the

air and soil. Plants take up nitrogen in its various forms from air and soil, and return it to animals in their food. This circulation of nitrogen is called the 'nitrogen cycle,' and is illustrated in the accompanying diagram

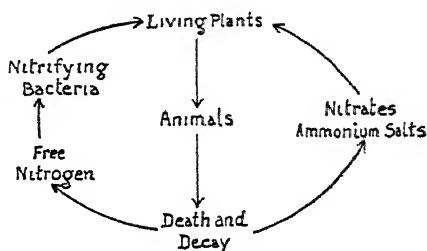


FIG 71 —The Nitrogen Cycle

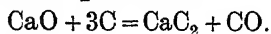
These natural methods of supplying the nitrogen required for

the growth of plants are not nearly sufficient to maintain good crops on cultivated land. It is necessary to add manure, organic matter containing nitrogen, or artificial fertilisers to supply nitrates and ammonium salts. These additions make the difference between starvation and plenty.

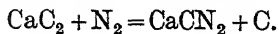
Twenty-five years ago, the world depended for its supply of artificial fertilisers mainly upon ammonium sulphate from gas-works and nitrate from Chile. The first of these is a comparatively small source of supply, and the deposits of Chile saltpetre cannot last indefinitely, consequently a failure or shortage of these supplies might mean widespread starvation. However, the utilisation of the nitrogen of the atmosphere for the manufacture of ammonia and of nitric acid has ensured a plentiful supply of artificial fertilisers for all time.

The most successful process is that perfected by F. Haber, a German chemist, in 1914, for the synthesis of ammonia from nitrogen and hydrogen. The nitrogen is obtained by the fractional distillation of liquid air. The hydrogen is obtained from water gas, a mixture of hydrogen, carbon monoxide and carbon dioxide. Water gas is mixed with steam and passed over heated oxide of iron, the carbon monoxide is oxidized to carbon dioxide, which is absorbed by caustic soda. The gases are mixed in the proportion of 3 volumes of hydrogen to 1 volume of nitrogen, and passed, under a pressure of 200 atmospheres, through a steel tube which is electrically heated to 500°. This tube contains some substance which acts as a catalyst in helping the combination of the gases. Iron, tungsten or molybdenum with small quantities of other metals and oxides are generally used. The gases leaving the apparatus contain 10% of ammonia, which is absorbed by passing through water, and the unchanged gases are again compressed and passed through the heated tube. Later forms of the process use greater pressures and higher temperatures and give a bigger yield.

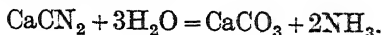
Another process of nitrogen fixation is the Frank-Caro or 'cyanamide' process. When lime and coke are heated together calcium carbide is produced :



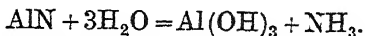
Calcium carbide heated strongly in nitrogen forms calcium cyanamide, CaCN_2 , mixed with carbon :



This product is either used as a fertiliser under the name of 'nitrolim,' or its nitrogen is converted into ammonia by treatment with superheated steam :



A third method, the Serpek process, consists in heating aluminium in nitrogen to obtain the nitride, AlN , and treating this with water :



Properties. Ammonia is a colourless gas with a distinctive odour. It is easily liquefied by compression and cooling. The boiling point of liquid ammonia is -33°C . When liquid ammonia vaporizes heat is absorbed, that is, heat is taken away from its surroundings.

Expt.—Put about an inch of strong ammonia solution into a beaker and place it upon a block of wood wetted with a little water. Take a long glass tube and blow through the ammonia, the beaker will in a short time be frozen to the block.

This property is made use of in ice-making and refrigeration.

Gaseous ammonia is fed into the pump *A*, compressed, and condensed in *B*, where the heat produced as the gas liquefies is carried away by cold water surrounding the pipe. The liquid ammonia then flows into the expansion coils immersed in brine or calcium chloride solution in vessel *C*. In these coils the liquid evaporates, absorbing heat from the brine and cooling it below zero. Water contained in the vessels *D* is frozen,

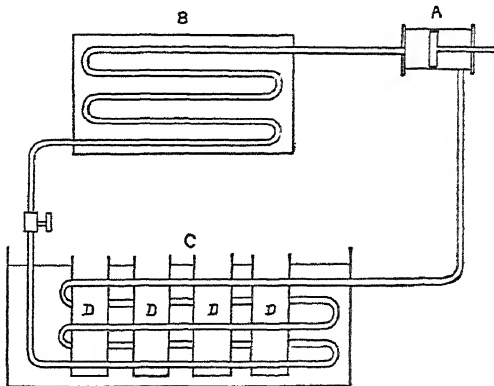


FIG 72 —Refrigeration.

but as brine has a lower freezing point than water it remains liquid. The gaseous ammonia then passes back to the pump

and the process is thus continuous. In cold-storage rooms the brine circulates in pipes round the walls and keeps the air cold.

Ammonia gas is very soluble in water. At 20°C . one volume of water dissolves 700 volumes of ammonia.

EXPT—Fit up the apparatus as shewn in the diagram. *A* is a round-bottom flask with a single-hole stopper carrying a glass tube drawn to a fine jet. The other end of the tube dips into water coloured with red litmus contained in the flask *B*. The stopper of *B* is also fitted with a side tube *D*. Fill flask *A* with ammonia and place in position, then blow into *D* to force a few drops of water into *A*. The ammonia dissolves creating a partial vacuum, the water is sucked up and plays like a fountain from the jet, the colour changes to blue, showing that the ammonia solution has an alkaline reaction. See also Fig. 84.

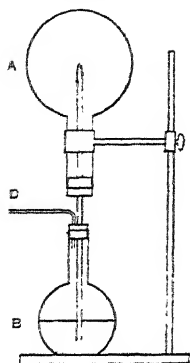
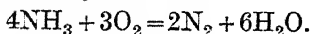


FIG. 73—Ammonia Fountain

The rapidity of solution may also be shown by immersing the open end of a small jar of ammonia in water. The action is so violent that the jar is sometimes broken, so if the experiment is attempted the hand should be protected with a cloth.

Ammonia is not a supporter of combustion, a lighted taper burns only for a moment in the gas with a greenish-yellow flame. Ammonia does not burn in air but burns readily in an atmosphere of oxygen. The diagram shows a method of demonstration. A current of ammonia gas is obtained by warming ammonia solution in flask *C*. Tube *B* is connected with a cylinder or gas-holder of oxygen, and gives an atmosphere of oxygen in *A*. A layer of cotton wool at the bottom of *A* helps to spread the stream of oxygen. When a light is applied the ammonia burns with a greenish-yellow flame.



Ammonium nitrate, NH_4NO_3 , and ammonium nitrite, NH_4NO_2 , are also formed. A mixture of ammonia and oxygen in the above proportions explodes when ignited.

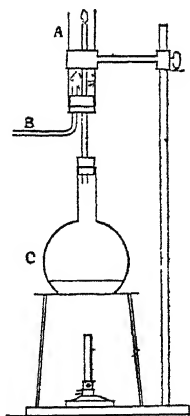
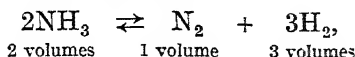


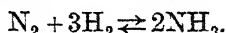
FIG. 74.

If a current of oxygen be passed through concentrated ammonia solution and a hot spiral of platinum wire be suspended in the mixture, the wire will glow red hot and the ammonia will be oxidized. Too rapid a stream of oxygen may cause explosions. The products of oxidation are the same as above.

Composition. Berthollet (1785) found that if electric sparks are passed through gaseous ammonia, the volume becomes nearly doubled. The gas is split up into nitrogen and hydrogen.



A small quantity, about 2%, remains undecomposed as the reaction is reversible, that is, ammonia may be also formed by sparking a mixture of nitrogen and hydrogen.



The experiment is performed in a eudiometer. After sparking the ammonia, oxygen is added in excess to combine with the hydrogen, a spark is passed and water is formed. The contraction is due to the disappearance of the hydrogen (the volume occupied by the water is negligible) carrying with it half its volume of oxygen. Thus $\frac{2}{3}$ of the contraction represents the volume of the hydrogen.

Example.

Volume of ammonia taken	-	-	-	18 c.c.
Volume of gas after sparking	-	-	-	35.7 c.c.
Volume after adding oxygen	-	-	-	116.2 c.c.
Volume after explosion	-	-	-	76 c.c.
The contraction is	-	-	-	40.2 c.c.

The volume of the hydrogen is then $\frac{2}{3}$ of 40.2 c.c. or 26.8 c.c., and the volume of the nitrogen is $35.7 - 26.8 = 8.9$ c.c. Hence 18 c.c. of ammonia give 8.9 c.c. of nitrogen and 26.8 c.c. of hydrogen, or two volumes of ammonia give one volume of nitrogen and three volumes of hydrogen. According to Avogadro's law, equal volumes contain equal numbers of molecules, hence two molecules of ammonia give one molecule of

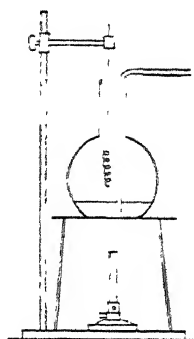
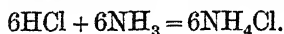
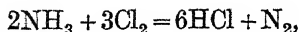


FIG 75

nitrogen and three molecules of hydrogen. As the nitrogen and hydrogen molecule each consists of two atoms, one molecule of ammonia contains one atom of nitrogen and three atoms of hydrogen and the formula is NH_3 .

Another method, but a less accurate one, of demonstrating the composition of ammonia is due to Hofmann (1865). When ammonia is treated with chlorine, the chlorine combines with the hydrogen to form hydrochloric acid and sets free nitrogen. The hydrochloric acid unites with ammonia giving ammonium chloride,



Expt.—Take a long glass tube, fit it with a cork carrying a dropping funnel and divide it into three equal parts marked by rubber bands. Fill the tube with chlorine. Pour some strong ammonia solution into the funnel and let it run, drop by drop, into the chlorine. Each drop is attended by a flash of light, and white clouds of ammonium chloride are formed. When sufficient ammonia has been added, run in some dilute sulphuric acid to combine with the excess, and shake. Fill the funnel with water and fit to it by a cork a syphon tube, also filled with water, the other end dipping into water in a beaker. On opening the stop-cock water will run into the tube up to the second mark. The remaining gas, which occupies $\frac{1}{3}$ of the original volume, is nitrogen.

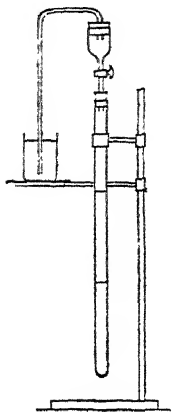
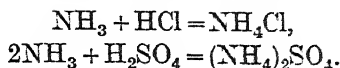


Fig 76.—Hofmann's Method.

Thus three volumes of chlorine react with ammonia, giving one volume of nitrogen, and three volumes of chlorine combine with three volumes of hydrogen; therefore the ammonia produced one volume of nitrogen and three volumes of hydrogen. The molecule of ammonia must then contain nitrogen and hydrogen atoms in the proportion of 1 : 3. We do not know the volume of ammonia which has been decomposed, and can only infer that the molecule must be some multiple of NH_3 , so we write it meantime $(\text{NH}_3)_x$. By measurement the relative density of ammonia is found to be 8.5, hence its molecular weight is 17. The formula must then be NH_3 , as the sum of the weight of the atoms is 17.

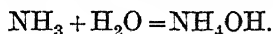
The composition of ammonia may also be shown by the electrolysis of a strong solution. A small quantity of ammonium sulphate is added to render the solution conducting. Nitrogen and hydrogen are given off at the electrodes in the proportion of one volume of nitrogen to three volumes of hydrogen.

Ammonium Compounds. Ammonia combines with acids to form salts, which are all soluble in water.



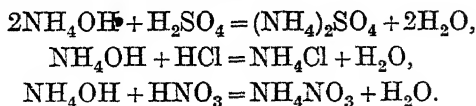
In these, the group of atoms NH_4 acts as a positive monovalent radical. Its salts resemble those of sodium, so NH_4 is called 'ammonium,' ending in 'ium' like sodium, potassium and magnesium. Though ammonium acts like a metal in forming salts, it has not been isolated, and it is doubtful whether it can exist independently. When a little sodium amalgam, an alloy of sodium and mercury, is added to a concentrated solution of ammonium chloride it swells up, forming a frothy mass which gradually decomposes, giving off ammonia and hydrogen in the ratio $2\text{NH}_3 : \text{H}_2$. When ammonium amalgam is added to copper sulphate solution some copper is precipitated and ammonium sulphate is formed. These facts seem to indicate that ammonium, though extremely unstable, can actually exist.

Ammonium hydroxide. When ammonia is dissolved in water, the solution contains ammonium hydroxide,



This substance can be obtained as a crystalline solid melting at -79°C . Ammonia solution, or ammonium hydroxide as it is generally called, has basic properties and is strongly alkaline to litmus. It smells of ammonia, and on boiling all the dissolved gas is expelled. Perfectly dry ammonia does not contain the OH group characteristic of alkalies, and does not react with dry litmus paper.

Ammonium salts. If an acid be added to ammonium hydroxide until the solution is neutral to litmus, the corresponding salt is obtained on evaporation.



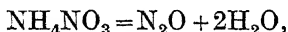
Ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$, is obtained from the 'gas liquor,' in the manufacture of coal gas. It is a white crystalline solid and is principally used as a fertiliser and in the production of other ammonium compounds. On heating it gives off ammonia.

Ammonium chloride, NH_4Cl , is made by mixing ammonia solution with hydrochloric acid or by passing ammonia gas into hydrochloric acid solution. When the substances are brought together in the gaseous state, white fumes of ammonium chloride are formed.

EXPT.—Hold a glass rod dipped in concentrated hydrochloric acid over an open ammonium hydroxide bottle.

Ammonium chloride is made commercially from ammonium sulphate by boiling with common salt, and crystallising the solution fractionally. It is a white crystalline substance and can be purified by sublimation. Ammonium chloride is used in the textile industries, and as a flux to remove oxide from metallic surfaces in soldering and in galvanising iron.

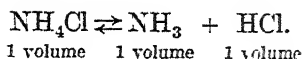
Ammonium nitrate, NH_4NO_3 , is made by neutralising nitric acid with ammonium hydroxide. It is like the other ammonium salts white and crystalline. On heating, it decomposes into water and nitrous oxide, and is chiefly used in making nitrous oxide and



in the manufacture of fireworks and explosives. A powerful explosive known as *ammonal* consists of a mixture of ammonium nitrate and powdered aluminium. Another, composed of ammonium nitrate and T.N.T. (tri-nitro-toluene) is called *amatol*. When ammonium nitrate is dissolved in ice-cold water in the proportion of 3 parts to 5 of water, the temperature falls to -15°C . A mixture of ammonium nitrate and ice thus makes a good freezing mixture. Try the experiment.

Dissociation. We have seen that the value of the vapour density of a gas is half its molecular weight. Adding together the weights of the constituent atoms of ammonium chloride, NH_4Cl , we get $14 + 4 + 35.5 = 53.5$, hence its vapour density should be 26.7. But experiment shows that it is really only half that value. The explanation is that on heating, ammonium chloride breaks up into ammonia and hydrochloric acid,

which re-combine on cooling. This is another example of a reversible reaction,



Thus the mixed gases occupy twice the volume they would have occupied had there been no dissociation, and the vapour density is consequently halved. This accords with the experimental result. When a substance breaks up on heating but does not recombine on cooling the process is called *decomposition*, when the products unite again on cooling, it is termed *dissociation*.

EXPT.—To show the *dissociation* of ammonium chloride. Take a glass tube of about $\frac{1}{2}$ -inch bore and open at both ends. Place in the centre some ammonium chloride plugged in with preheated asbestos fibre. Clamp the tube on a retort stand in a sloping position, and insert near the upper end a piece of moist red litmus paper and near the lower end a piece of blue paper. Heat the ammonium chloride with the Bunsen till it dissociates. The denser hydrochloric acid does not diffuse so rapidly and turns the blue litmus red, while the lighter ammonia diffuses more quickly into the upper part of the tube and turns the red litmus blue.

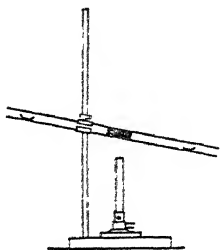
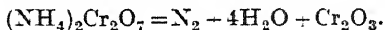


FIG 77

EXPT.—To show the *decomposition* of ammonium dichromate, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$. Powder a little of the salt and heat it in an iron dish. It burns brilliantly, setting free nitrogen and steam and leaving a fluffy mass of chromic oxide.



Tests for Ammonia and Ammonium Salts

1. Ammonia is readily recognised by its characteristic smell.
2. It turns moist red litmus paper blue.
3. It gives white fumes with hydrochloric acid gas.
4. Nessler's test. Add potassium iodide solution to a solution of mercuric chloride till the precipitate formed just redissolves, and make alkaline with sodium hydroxide. This is known as *Nessler's solution*, and is a very delicate test for ammonia, with which it gives a yellow or brown coloration or precipitate according to the quantity of ammonia present.

5. When a salt of ammonium is warmed with sodium hydroxide ammonia is evolved.

6. To test a solution for small quantities of ammonium salts, add some sodium hydroxide and distil, test the distillate with Nessler's reagent.

Additional Experiments

EXPT.—Make nitrogen by passing ammonia over heated copper oxide.

EXPT.—Prepare ammonia by heating ammonia solution with the addition of a small quantity of caustic soda. Also by heating an ammonium salt with caustic soda.

EXPT.—Add ammonium hydroxide solution, drop by drop, to a solution of copper sulphate. Observe the formation of a blue precipitate which finally dissolves to a blue solution.

EXPT.—To show the instability of ammonium hydroxide. Boil some dilute ammonium hydroxide in a flask till the vapour ceases to colour moist litmus paper and the liquid when poured into a little copper sulphate solution in a test tube gives no reaction.

EXPT.—Oxidation of ammonia. Place some strong ammonia solution in a flask. Warm gently, and bubble oxygen through it *slowly*. Heat a spiral of platinum wire to redness and suspend it in the flask. It continues to glow. Observe brown fumes of nitrogen peroxide. The solution is afterwards found to contain ammonium nitrate. This experiment may also be performed by taking a cylinder of ammonia gas, uncovering to let a little ammonia out and a little air in, and introducing the heated spiral.

EXPT.—Examine the action of heat on ammonium salts. Heat small quantities of the chloride, nitrate, sulphate, and phosphate in sublimation tubes.

EXPT.—To make ammonium sulphate. Add ammonium hydroxide to a mixture of equal parts of sulphuric acid and water till the solution is neutral. Evaporate to crystallisation. Boil a portion of the salt with sodium hydroxide and test for ammonia. Dissolve another portion in water and add barium chloride solution, getting a white precipitate of barium sulphate.

QUESTIONS

1. Describe a laboratory method for the preparation of pure nitrogen. Nitrogen derived from the air by removal of oxygen has a density of 14.070, whereas nitrogen obtained from a com-

pound containing nitrogen has a density of 14.005. Explain the discrepancy. (Scot. Leaving Cert.)

2. Explain how nitrates are produced by natural agencies. How can free nitrogen be converted into nitric acid? Write some account of the action of metals upon this acid.

(Oxford and Camb. School Cert.)

3. How is ammonia prepared? Draw the form of apparatus used to prepare and collect a jar of the gas, and describe experiments to show its alkaline properties and solubility in water. Explain how ammonia may be oxidized to nitric acid.

(Oxford and Camb. School Cert.)

4. Describe the method you would employ to prepare a jar of dry ammonia. A given volume of ammonia is approximately doubled on sparking. If now an excess of oxygen is added to the mixed gases and the sparking is repeated, contraction takes place. Thus an experiment yielded the following results:

Volume of ammonia	-	-	-	15 c.c.
Volume after sparking	-	-	-	29.9 c.c.
Volume after adding oxygen	-	-	-	108.1 c.c.
Volume after sparking	-	-	-	74.7 c.c.

Explain fully all that has happened, and calculate the composition of ammonia. What other information would you require before you could write the formula of the gas? (Scot. Leaving Cert.)

5. If you were given some ammonium nitrate, how would you prepare from it and collect (a) an oxide of nitrogen, (b) ammonia. (c) nitrogen? Give equations. (London Matric.)

6. Write an essay extending to not more than one page and a half, on the part played by carbon dioxide and by nitrogen in animal and plant life. Indicate by diagrams the carbon and nitrogen cycles in nature. (Scot. Leaving Cert.)

CHAPTER XXIV

OXYGEN COMPOUNDS OF NITROGEN

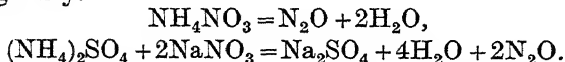
NITROGEN forms five oxides.

Nitrous oxide	-	-	-	-	-	-	N_2O
Nitric oxide	-	-	-	-	-	-	NO
Nitrogen trioxide, the anhydride of nitrous acid	-	-	-	-	-	-	N_2O_3
Nitrogen peroxide or tetroxide	-	-	-	-	-	-	NO_2 or N_2O_4
Nitrogen pentoxide, the anhydride of nitric acid	-	-	-	-	-	-	N_2O_5

If nitric oxide be written N_2O_2 , observe that the number of atoms of oxygen, which unite with two atoms of nitrogen, increases regularly from one to five, a good illustration of the law of multiple proportions.

Nitrous Oxide. Priestley first made this gas in 1772, by reducing nitric oxide, NO , with moist iron filings. In 1799, Sir Humphry Davy prepared it by heating ammonium nitrate and determined its composition.

Preparation. This is still the most convenient method of obtaining it, but as the decomposition is sometimes explosive, it is better to use a dry mixture of ammonium sulphate and sodium nitrate, with which the reaction proceeds more slowly and regularly.

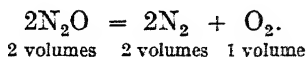


The ammonium nitrate or mixture of ammonium sulphate and sodium nitrate is heated in a flask with delivery tube and the gas is collected over warm water as it is rather soluble in cold water.

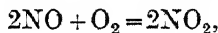
EXPT.—Prepare some nitrous oxide and apply the following tests :

1. Note the faint sweetish smell.
2. Test the ability of the gas to support combustion by introducing burning sulphur, a glowing chip, a piece of phosphorus.

Properties. Nitrous oxide is a colourless gas with a faint sweet odour. At ordinary temperatures 100 volumes of water will dissolve 70 volumes of the gas. Its density is 22. It can be condensed to a liquid, B.P. 89° C. It is a better supporter of combustion than air. A burning substance introduced into nitrous oxide must give out sufficient heat to decompose it into nitrogen and oxygen, it then continues to burn in the oxygen set free. Thus feebly burning sulphur is extinguished while a glowing splinter and a piece of phosphorus burn more brightly, because nitrous oxide gives on decomposition $\frac{1}{2}$ of its volume of oxygen, while air contains only $\frac{1}{5}$.



It is possible to mistake nitrous oxide for oxygen, but they can be readily distinguished by the smell, the solubility, and the change of colour of oxygen on adding to it nitric oxide, NO. Oxygen with nitric oxide gives a brown gas, nitrogen peroxide,



with nitrous oxide oxygen gives no change.

When inhaled, nitrous oxide produces unconsciousness, and is used as an anaesthetic in dentistry. Small quantities may cause hysterical laughter, which has given rise to the name 'laughing gas.' Davy says that after breathing the gas he 'danced about the laboratory as a madman.' For use as an anaesthetic, nitrous oxide must be freed from nitric oxide and other impurities by passing it through sodium hydroxide and ferrous sulphate solutions.

Composition. Potassium burns in nitrous oxide combining with the oxygen and liberating nitrogen. Davy determined its composition by this method, confining the gas over mercury, and found that the volume is unchanged, that is, one volume of nitrous oxide gives one volume of nitrogen.

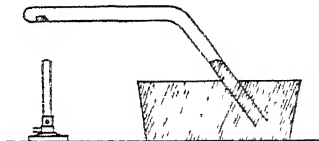
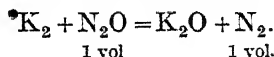


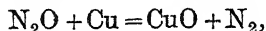
FIG 78 —Davy's Method



By Avogadro's law, therefore, one molecule of nitrous oxide

contains one molecule of nitrogen, and its composition is N_2O_x . Determination of its vapour density gives the value 22, consequently the molecular weight is 44. Two atoms of nitrogen weigh 28, which subtracted from 44 leaves 16, the weight of one atom of oxygen, and the formula must be N_2O .

By another method, a measured volume of nitrous oxide is passed through a tube containing heated copper. The copper combines with the oxygen to form copper oxide,

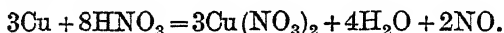


and the increase of weight shows the amount of combined oxygen. The graphic formula of nitrous oxide is generally

given as $\begin{array}{c} \text{N} \\ \parallel \\ \text{N} \end{array} \text{O}$, in which the nitrogen atom is trivalent.

Nitric Oxide, NO. Mayow (1669) and Boyle (1671), both made nitric oxide, but its discovery is generally ascribed to Priestley (1772), as it was he who first investigated its properties.

Preparation. It is prepared by the action of dilute nitric acid on copper :



EXPT.—Prepare nitric oxide. Fit up a flask with bulb tube and delivery tube to collect the gas over water.

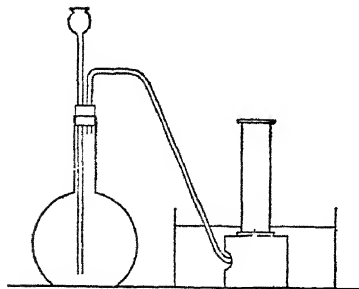


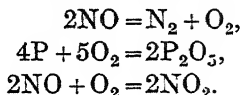
FIG. 79.

Place some copper in the flask and pour into the funnel a mixture of equal parts of strong nitric acid and water. A brown vapour first appears in the flask due to the combination of nitric oxide with oxygen forming nitrogen peroxide, which dissolves in the water. The gas should be collected at once, as after the action has proceeded for some time nitrous oxide and nitrogen are formed.

A purer gas is obtained by taking a mixture of one part of potassium nitrate with six parts of ferrous sulphate and six parts of water. Add a little concentrated sulphuric acid and warm.

Properties. Nitric oxide is a colourless gas. At 18°C . 100 volumes of water dissolve 5 volumes. It readily unites with

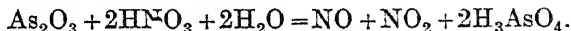
oxygen, so that neither its smell nor its physiological action can be determined. No other gas gives brown fumes with oxygen. Its vapour density is 15 and its B.P. is -150°C . Nitric oxide is absorbed by ferrous sulphate, giving a dark brown solution which contains $x\text{FeSO}_4 \cdot y\text{NO}$, the composition varying with the temperature. On warming this solution nitric oxide is evolved, another method of obtaining the pure gas. Nitric oxide is inferior to nitrous oxide as a supporter of combustion. Only substances which on burning give out sufficient heat to decompose the gas will continue to burn in it. Burning sulphur is extinguished, while strongly burning phosphorus burns more brilliantly, forming white clouds of phosphorus pentoxide mixed with brown vapour of nitrogen peroxide. The nitric oxide is decomposed into nitrogen and oxygen, the oxygen combines with the phosphorus and part of it also with the excess of nitric oxide.



Composition. The methods used to determine the composition of nitrous oxide are also applicable to nitric oxide. Davy's method of heating potassium in a measured volume of the gas, shows that one volume of nitric oxide gives $\frac{1}{2}$ volume of nitrogen. Hence one molecule of nitric oxide contains half a molecule or one atom of nitrogen. The molecule is then NO_x . The vapour density is 15, and the molecular weight is 30. The weight of an atom of nitrogen is 14, which subtracted from 30 leaves 16, the weight of an atom of oxygen. The formula is consequently NO . The readiness with which nitric oxide combines with oxygen to form NO_2 , and with chlorine to form nitrosyl chloride, NOCl , leads us to believe that the graphic formula is --N=O , shewing a free valence.

Nitrogen Trioxide or nitrous anhydride, N_2O_3 .

Preparation. When a mixture of nitric oxide and nitrogen peroxide is cooled to -30°C . nitrogen trioxide condenses as a bluish liquid. This mixture may be produced by heating arsenious oxide with nitric acid :



With rise of temperature it dissociates :

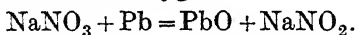


Nitrogen trioxide with cold water forms nitrous acid, and is consequently regarded as the anhydride of nitrous acid.



Its graphic formula may be $\text{O} \begin{array}{c} \diagup \text{N} = \text{O} \\ \diagdown \text{N} = \text{O} \end{array}$.

Nitrites. Nitrous acid, HNO_2 , forms salts known as nitrites. Sodium and potassium nitrites are the best known of these. They are made by the action of heat on the respective nitrates, generally with the addition of a metallic reducing agent such as lead, to help to remove oxygen :

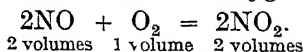


If equal weights of lead filings and sodium nitrate be heated in a crucible, sodium nitrite, NaNO_2 , is produced. It is dissolved out of the residue by cold water, the solution is filtered and evaporated to obtain the salt.

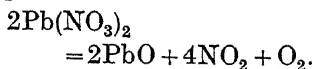
Properties. Nitrites are decomposed by dilute sulphuric acid, giving brown fumes. They can thus be distinguished from nitrates, which give brown fumes with concentrated sulphuric acid only. They also liberate iodine from potassium iodide in the presence of dilute acid. Nitrites are oxidized to nitrates by potassium permanganate. The graphic formula of nitrous acid is probably $\text{O} = \text{N} - \text{O} - \text{H}$.

Nitrogen Peroxide or Tetroxide, NO_2 . The distinctive red-dish brown colour of this gas was observed by many early chemists, but Gay Lussac (1816) was the first to determine its composition.

Preparation. As already seen, this gas is formed by the union of two volumes of nitric oxide with one volume of oxygen :



It may be prepared by heating lead nitrate.



EXPT.—Heat some dry lead nitrate in a test tube and pass the gas through a U-tube cooled in a freezing mixture of ice and salt. Oxygen is produced at the same time and its presence may be shown by holding a glowing

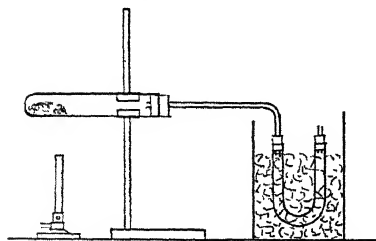
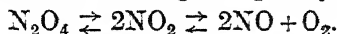


FIG 80

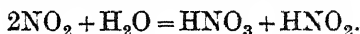
in a freezing mixture of ice and salt. Oxygen is produced at the same time and its presence may be shown by holding a glowing

wood splint above the exit of the U-tube. Nitrogen peroxide is obtained as a yellow liquid.

Properties. Nitrogen peroxide is a volatile liquid at ordinary temperatures, giving off a brown vapour. When cooled it freezes, forming colourless crystals, melting at -9°C . to a pale yellow liquid. When this liquid is heated it darkens in colour and boils at 26° , forming a brown vapour which has a density of about 38, indicating that it consists mainly of N_2O_4 . On further heating, the colour of the gas deepens and the vapour density decreases, showing that the molecule N_2O_4 has been partly dissociated into NO_2 . At 140° it is practically black, and the density has fallen to 23—that is, the gas consists wholly of NO_2 molecules. At higher temperatures NO_2 begins to dissociate into nitric oxide and oxygen, and the gas becomes colourless. On cooling all these changes take place in the reverse order. The equations which represent them are called reversible equations, as they can proceed forwards or backwards, and instead of the usual sign of equality the sign \rightleftharpoons is used.

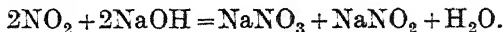


Nitrogen peroxide is a poisonous gas, and great care should be taken to avoid breathing it. Even a small quantity in the atmosphere causes headache and sickness. Like the other oxides of nitrogen, it is not combustible, and only supports the combustion of substances which give out sufficient heat on burning to decompose the gas. It is absorbed by cold water, giving a mixture of nitric and nitrous acids :

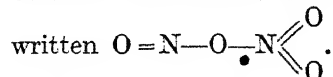


With warm water the nitrous acid decomposes into nitric acid and nitric oxide : $3\text{HNO}_2 = \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}$.

Alkalis also absorb nitrogen peroxide, giving a mixture of nitrate and nitrite :



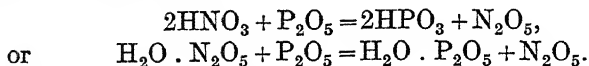
Thus nitrogen peroxide may be regarded as a mixed anhydride of nitric and nitrous acids, and its graphic formula may be



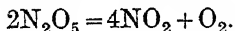
Nitrogen Pentoxide or nitric anhydride, N_2O_5 .

Preparation. This substance is obtained as an orange-

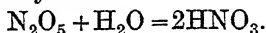
coloured liquid, when a mixture of concentrated nitric acid and phosphorus pentoxide is distilled. The distillate separates into two layers, the upper of which is removed and cooled in ice water. Nitrogen pentoxide separates out as a white crystalline solid. The phosphorus pentoxide, owing to its strong attraction for water, has removed the elements of water from the nitric acid.



Properties. When solid nitrogen peroxide is heated it melts and decomposes explosively into nitrogen peroxide and oxygen:



It reacts with water, giving nitric acid, and is consequently regarded as nitric anhydride:



Nitric Acid. The great Arabian chemist, Geber, was the first to describe the preparation of nitric acid, by distilling a mixture of saltpetre and alum with copperas (ferrous sulphate) Glauber (1650) obtained it by the action of sulphuric acid upon saltpetre. Lavoisier (1776) showed that the acid contained oxygen and nitrogen, and Gay-Lussac (1816) determined its composition quantitatively. Its old name, which still survives, is aqua fortis, or strong water, given it on account of its powerfully corrosive action upon many substances.

Preparation. Nitric acid is prepared in the laboratory by distilling a mixture of equal weights of potassium nitrate and concentrated sulphuric acid.

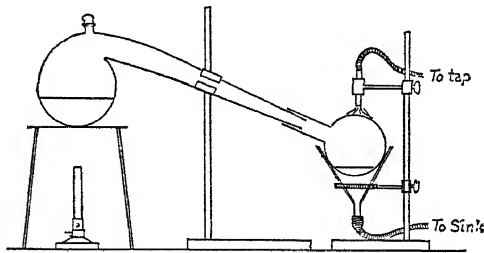
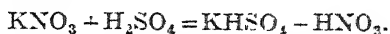


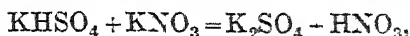
FIG 81.

EXPT.—Place in a glass retort some saltpetre and introduce an equal weight of strong sulphuric acid. Support the retort upon a

wire gauze. Heat the mixture, and collect the acid in a glass receiver cooled by a stream of water. At the usual temperature of heating the action is :



At a higher temperature there is the further reaction .



but much of the acid is decomposed. The same process is made use of in the commercial production of nitric acid. Sodium nitrate, which is found in Chile as a natural product, is used, and the distillation is carried out in cast-iron retorts. The acid is condensed in cooled stoneware receivers.

Nitric acid prepared in this way has a yellow colour due to the presence of nitrogen peroxide resulting from decomposition of the acid. 'Fuming nitric acid' is brown in colour and contains a considerable amount of nitrogen peroxide in solution.

H. Cavendish (1785) showed that nitric acid can be produced by passing electric sparks through a mixture of oxygen and nitrogen. Nitrogen peroxide is formed, which, if water be present, dissolves, giving nitric and nitrous acids. Towards the end of last century it became evident that with the increasing consumption of nitric acid the deposits of the natural product 'Chile saltpetre' or sodium nitrate could not last indefinitely. As the world was completely dependent upon this substance for the manufacture of nitric acid, chemists applied themselves to the discovery of methods of utilising atmospheric nitrogen for this purpose. Their efforts were completely successful, and resulted in the invention of several well-known processes for the fixation of atmospheric nitrogen. Some of these have already been described in connection with ammonia. Two which are used in the production of nitric acid are :

1. The Birkeland and Eyde process.
2. The ammonia oxidation process in combination with the Haber process.

The Birkeland-Eyde process is a development of Cavendish's experiment. Air instead of being sparked is brought in contact with an electric arc. The furnace consists of a flat circular steel box, somewhat resembling a coin in shape and lined with fire brick. The box contains two electrodes, between which an electric arc is maintained, forming a circular sheet of flame

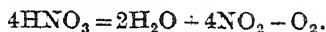
6 feet in diameter. The temperature of the flame is 3000° – 3500° C. Air is drawn into the furnace and is partly converted into nitric oxide. The gases leaving the furnace pass through cooling chambers and then through absorption towers, where the nitric oxide is oxidized to nitrogen peroxide and dissolves in water, giving nitric and nitrous acids. This process has, however, been found to be too expensive, and the factories working it in Norway have changed over to the manufacture of ammonia from hydrogen and nitrogen.

The ammonia oxidation process was invented by W. Ostwald, a German chemist. Ammonia gas and air are passed through a screen of platinum gauze heated electrically to 800° C., and 85% of the ammonia is converted into nitric oxide, which is oxidized to nitrogen peroxide and absorbed in water, giving nitric and nitrous acids. The platinum acts as a catalyst.

The Haber process combined with the ammonia oxidation process has already left its mark upon the world's history. The Great War of 1914-1918 has with considerable truth been called 'a chemists' war.' Nitric acid is indispensable for the manufacture of explosives, and had these processes not been perfected just at that time, Germany, isolated as she was, could not have obtained sufficient Chile saltpetre to supply her needs. These inventions enabled her to make as much nitric acid as she required within her own borders. France later followed suit. Fortunately for our country, she had latterly the command of the seas, and could obtain Chile nitrate, as at the end of the War, although the ammonia oxidation process was worked, there was not a single nitrogen fixation factory in Britain. Since these days, however, factories have been built for the production of ammonia from atmospheric nitrogen.

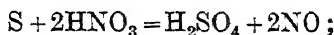
Properties of Nitric Acid. Pure nitric acid is a colourless liquid which fumes strongly in air. Its specific gravity is 1.5. Its boiling-point is 86° C., and it can be frozen to a white solid which melts at -47° C. It mixes in all proportions with water, and a solution containing 68% of the acid boils at 120° C. and distils unchanged; this is known as 'constant boiling acid.' A more dilute solution loses water on boiling, and a more concentrated solution loses acid until it attains a strength of 68%, when it boils unchanged. Its specific gravity is 1.4. At high temperatures nitric acid decomposes into nitrogen peroxide and oxygen.

EXPT.—Take a silica flask and fit it with a dropping funnel and a leading tube to collect the oxygen over water. Pour some nitric acid into the bulb and heat the flask. Allow the acid to fall a drop at a time into the hot flask. Brown fumes of nitrogen peroxide appear; these dissolve in the water and oxygen can be collected. Note that only a silica or quartz flask will stand this harsh treatment. The equation is :



Nitric acid is a strongly corrosive liquid. Great care should be observed in using the concentrated acid. It stains the skin yellow and causes painful sores. A drop falling on the clothes destroys the material. In such a case plenty of dilute ammonia should be at once applied and the resulting ammonium nitrate afterwards washed out.

Strong nitric acid is a powerful oxidizing agent, as we might expect from the large proportion of oxygen which it contains. It oxidizes sulphur to sulphuric acid :



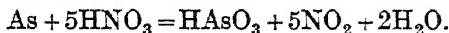
phosphorus to phosphoric acid :



iodine to iodic acid :

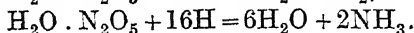
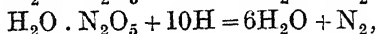
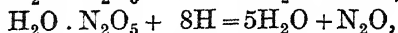
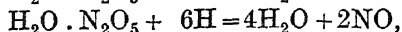
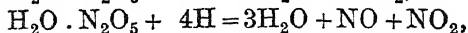
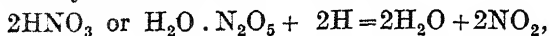


arsenic to arsenic acid :

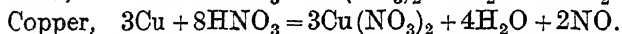
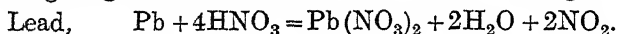


These equations may represent, generally speaking, the reactions which take place, but the kind and quantity of the oxides of nitrogen given off vary with conditions of temperature and concentration. When dilute hydrochloric and sulphuric acids act upon metals, hydrogen is usually evolved, but only with one or two metals—for example, magnesium and manganese—does dilute nitric acid give hydrogen. This behaviour is due to the oxidizing power of the acid. We may suppose that hydrogen is first produced and is immediately oxidized by the nitric acid, which is at the same time reduced to oxides of nitrogen or even to nitrogen or ammonia. The following equations show the possible products of reduction. In studying the reduction of nitric acid and similar compounds, it is helpful to

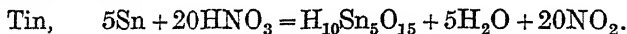
write the formula as a combination of water and the anhydride, as it is only the latter that is reduced.



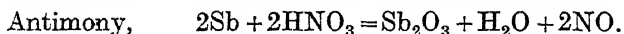
Observe that we are dealing here with atomic, not with molecular hydrogen. Molecular or free hydrogen may be passed through nitric acid without any reducing action, but at the moment when hydrogen is liberated from the acid, it is in the atomic or 'nascent' state, and has great chemical activity. The atoms, instead of combining with each other to form molecules, attack the nitric acid, abstracting oxygen and leaving various reduction products. Nitric acid dissolves most of the metals, giving a metallic nitrate and oxides of nitrogen.



Tin and antimony are not dissolved, but changed into white insoluble oxides.



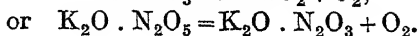
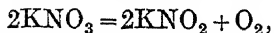
$\text{H}_{10}\text{Sn}_5\text{O}_{15}$ or $5\text{SnO}_2 \cdot 5\text{H}_2\text{O}$ is called metastannic acid, and when heated loses water, giving stannic oxide, SnO_2 .



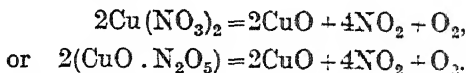
The oxides Sb_2O_4 and Sb_2O_5 may also be formed.

Gold and platinum are not dissolved by nitric acid. Hence nitric acid is used by goldsmiths to test the purity of gold, as it attacks copper and silver, with which the metal is frequently alloyed. One part of nitric acid mixed with three parts of hydrochloric acid is known as *Aqua Regia*, and dissolves both gold and platinum, owing to the chlorine set free.

Nitrates. Nitric acid is monobasic. It acts upon metallic oxides, hydroxides and carbonates, giving nitrates, which are all soluble salts. Nitrates decompose when heated. The nitrates of potassium and sodium give nitrates and oxygen



Most other nitrates give the oxide of the metal, nitrogen peroxide and oxygen :



As nitrates give up oxygen on heating, they are often used as oxidizing agents. Potassium nitrate or saltpetre and ammonium nitrate are used in the manufacture of explosives.

For the identification of nitrates the brown ring test is useful :

EXPT.—Pour a little potassium nitrate solution into a test tube and dissolve in it a small crystal of ferrous sulphate. Then hold the tube in a sloping position and pour down the side some concentrated sulphuric acid. A brown ring will form where the two layers meet. The sulphuric acid sets free nitric acid from the nitrate, and this is reduced by the ferrous sulphate to nitric oxide, which forms a brown compound with the ferrous sulphate.

Additional Experiments

EXPT.—Warm a few drops of concentrated nitric acid with indigo solution. It is decolorised.

EXPT.—Warm some sawdust in a dish and pour a few drops of concentrated nitric acid on it. Ignition takes place.

EXPT.—Test the effect of concentrated nitric acid on cork and rubber. Result shows that nitric acid should be distilled in a glass retort.

EXPT.—Test the action of strong and dilute nitric acid on magnesium, copper, zinc, aluminium, tin, lead and iron.

QUESTIONS

1. Give the names and formulae of the oxides of nitrogen. Describe briefly the preparation and properties of any two of them. (Scot. Leaving Cert)
2. How would you prepare and collect a quantity of nitrous oxide, using lime, sulphuric acid, ammonium chloride, and saltpetre? What experiments would you perform to distinguish the gas so obtained from a mixture of two volumes of nitrogen with one volume of oxygen? (London Matric.)

3. Describe the preparation of nitrogen peroxide, and state how you would obtain a specimen in the liquid form. How would you demonstrate (a) its action on water, (b) whether it supports combustion? Write a note on each of the reactions (a) and (b), and give equations. The vapour density of this oxide at various temperatures is shown in the following table:

26° C.	60° C.	100° C.	135° C.	140° C.
38.3	30.1	24.3	23.1	23.0

What is the significance of these figures? (Scot. Leaving Cert.)

4. How would you obtain nitric oxide in as pure a state as possible? How would you convert a jarful of the gas wholly into nitric acid? (Oxford and Camb. School Cert.)

5. Describe the laboratory method of preparing nitric acid. Detail two experiments you would perform to show two chemical properties of the acid, other than its acidity. How would you shew that nitric acid contains hydrogen, oxygen, and nitrogen? Write a short note on the manufacture of nitric acid from the air. (Scot. Leaving Cert.)

6. What would be formed if nitric acid were (a) mixed with a solution of caustic soda and the liquid evaporated to dryness, (b) diluted with water and poured on to copper turnings, (c) mixed with concentrated hydrochloric acid and warmed?

(London Matric.)

7. Mention two modern methods for the utilization of atmospheric nitrogen, and outline the conditions of successful working. (Scot. Univ. Entrance.)

CHAPTER XXV

BALANCING EQUATIONS

BEFORE we can write an equation to represent what takes place in a chemical reaction, we must know the reacting substances and the products of the reaction. The proper proportions of these have then to be discovered, so that the equation may be balanced. In doing so the following rules should be observed.

1. As atoms are neither destroyed nor split up in a chemical change, the number of atoms of each element taking part must be the same on each side of the equation.

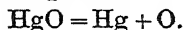
2. As the molecule is the smallest quantity of a substance which can have an independent existence, all substances should be represented in an equation by their molecules.

3. The molecule of the elementary gases, oxygen, hydrogen, nitrogen, chlorine, bromine vapour and iodine vapour contains 2 atoms, and is written in an equation O_2 , H_2 , N_2 , Cl_2 , Br_2 , I_2 .

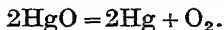
4. The molecules of the metallic elements and the molecules of the solid non-metallic elements (except iodine) are represented by the symbols; a figure in front of the symbol shews the number of molecules, for example, $2Fe$, $3C$, Zn , $4S$, $3P$, etc.

Methods of Balancing Equations

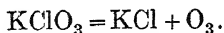
Example. Mercuric oxide on heating gives mercury and oxygen. Write the trial equation,



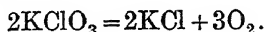
This is not in accordance with rules 2 and 3; we cannot have a single atom of oxygen. The simplest way to correct this is to multiply both sides of the equation by 2. This does not alter the proportions and gives oxygen in the molecular form, O_2 .



Example. Potassium chlorate, KClO_3 , on heating gives potassium chloride, KCl , and oxygen. Write the trial equation,

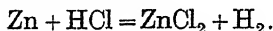


Rule 1 is satisfied, but not rules 2 and 3 ; O_3 does not represent molecular oxygen. As the molecule of oxygen is O_2 , we must have an even number of oxygen atoms, so multiply both sides of the equation by 2.

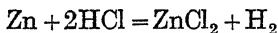


This gives 6 atoms or 3 molecules of oxygen.

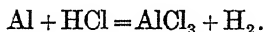
Example. Zinc dissolves in dilute hydrochloric acid, giving zinc chloride and hydrogen. Using the table which shews the valency of radicals, we find that the formula of zinc chloride is ZnCl_2 . Write the trial equation,



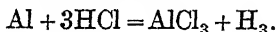
This equation breaks rule 1. There are 2 chlorine and 2 hydrogen atoms on the right, and only 1 of each on the left, so we must take 2 molecules of hydrochloric acid, which puts matters right.



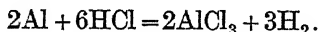
Example. Hydrochloric acid dissolves aluminium, giving aluminium chloride and hydrogen. From the table we find that aluminium is trivalent, so the chloride is AlCl_3 . Write the trial equation,



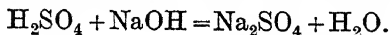
Rule 1 is broken. Three chlorine atoms are required on the left of the equation. Try 3HCl .



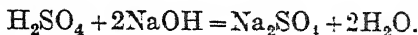
Rule 1 is now satisfied, but H_3 is not molecular hydrogen, so multiply each side by 2.



Example. Sulphuric acid neutralizes sodium hydroxide, giving sodium sulphate and water. The formulae are in order, H_2SO_4 , NaOH and Na_2SO_4 . Write the trial equation.



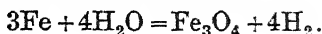
There are 2 sodium atoms on the right and 1 on the left, therefore take 2NaOH .



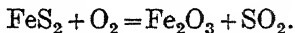
Example. When steam is passed over red-hot iron, an oxide of iron known as magnetic oxide, Fe_3O_4 , is formed, and the steam is reduced to hydrogen. Write the trial equation.



To obtain Fe_3O_4 , we must have on the left at least 3Fe and 4O . and we get this by writing the equation,



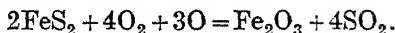
Example. Iron pyrites heated in air is oxidized to ferric oxide, Fe_2O_3 , and sulphur dioxide, SO_2 . Write the trial equation,



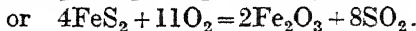
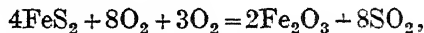
We require 2Fe on the left, and this brings in 4S , which needs 4O_2 to transform it into sulphur dioxide.



But we also require 3O for the 2Fe .



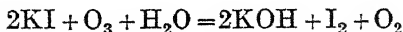
Now 3O does not represent molecular oxygen. therefore we must multiply both sides by 2.



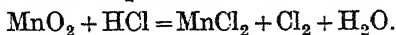
Example. Ozone, O_3 , liberates iodine from potassium iodide solution. KI . The products are potassium hydroxide, KOH , iodine, and oxygen. Write the trial equation.



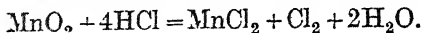
To obtain I_2 we must take 2KI , and as the hydrogen in the potassium hydroxide must come from water, we add a molecule of water.



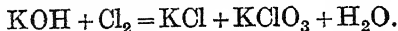
Example. Hydrochloric acid is oxidized by manganese dioxide, MnO_2 , giving manganous chloride, MnCl_2 , chlorine and water. Write the trial equation,



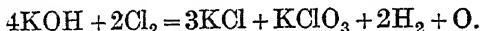
There are 4 chlorine atoms on the right, so we must have 4 on the left.



Example. Chlorine acts on potassium hydroxide, giving potassium chloride, KCl, potassium chlorate, KClO_3 , and water.



Four oxygen atoms on the right require 4 oxygen atoms on the left, that is, 4KOH; 3K must form 3KCl, otherwise we need more oxygen, so 4 chlorine atoms are required.

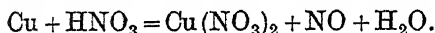


Another atom of oxygen is evidently required for the 2H_2 , but we cannot have 5KOH, as we must have an even number of hydrogen atoms to form water, therefore try 6KOH.

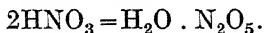


For the 6 potassium atoms we need 6 chlorine atoms.

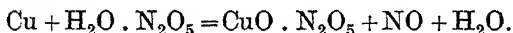
Example. Dilute nitric acid dissolves copper, giving copper nitrate, $\text{Cu}(\text{NO}_3)_2$, nitric oxide, NO, and water.



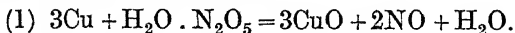
In balancing equations involving the reduction of nitric acid (here NO is obviously a product of reduction), it is often convenient to take two molecules and divide up into water and the anhydride.



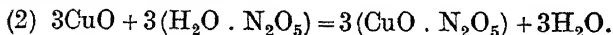
Write the equation accordingly, and treat the copper nitrate in the same way.



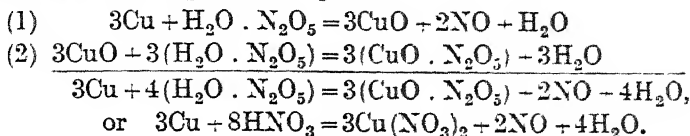
This shews the oxidizing action more clearly, Cu is oxidized to CuO, and N_2O_5 is reduced to NO. One molecule of nitric anhydride, N_2O_5 , will give 2NO and leave 3 oxygen atoms free to oxidize 3 copper atoms, thus:



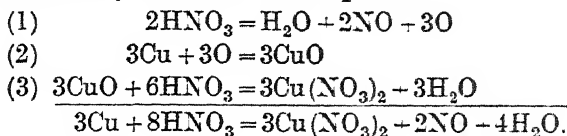
But the copper oxide combines with the excess of nitric acid to form copper nitrate, for which $3(\text{H}_2\text{O} \cdot \text{N}_2\text{O}_5)$ or 6 molecules of nitric acid are required.



Add these two equations together,

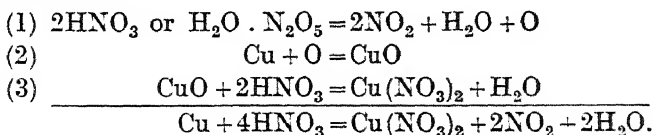


Using the ordinary formulae, the steps are :



This is a method generally in use for balancing complex equations. We may select two of the reacting substances and construct a 'partial' equation, giving one or more of the required products. Several of these 'partial' equations may be made, and any balances on the right are carried to the left and adjusted so that they cancel out when all the equations are added. This is a purely arithmetical method; the partial equations may not always be actual stages in the reaction, and for the purpose of calculation atoms may be used, as in the last example, without breaking our general rule.

Example. The action of concentrated nitric acid on copper gives copper nitrate, nitrogen peroxide, NO_2 , and water. Following the method of the preceding example, the partial equations are :

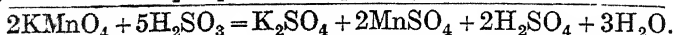
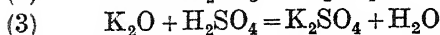
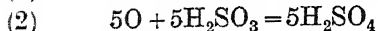
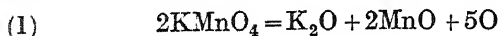


Example. Potassium permanganate, KMnO_4 , is reduced by sulphurous acid, giving products, potassium sulphate, K_2SO_4 , manganous sulphate, MnSO_4 , sulphuric acid, H_2SO_4 , and water. Take 2 molecules of KMnO_4 , and divide into oxides, supplying the metals with the quantity of oxygen required for the basic oxide.



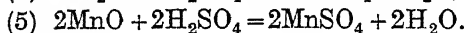
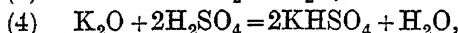
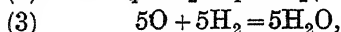
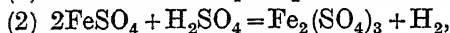
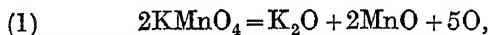
Thus we see that 5 atoms of oxygen are available for oxidation, and these will oxidize 5 molecules of sulphurous acid. Also the

oxides of potassium and manganese are converted into sulphates. Write the partial equations accordingly, and add them all together.

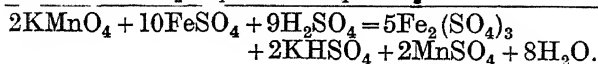
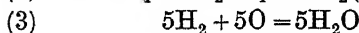
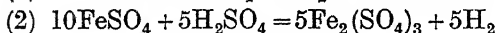


Example. A similar action is the oxidation of ferrous sulphate by permanganate in the presence of sulphuric acid. The products are potassium hydrogen sulphate, KHSO_4 , manganous sulphate, MnSO_4 , ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$ and water.

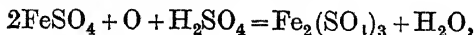
Write the partial equations :



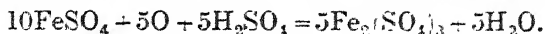
In equation 3, 5H_2 are required to unite with 5O , therefore equation 2 must be multiplied by 5, correct this and add all the partial equations :



Another method of working the above is to dissect 2FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ into their oxides, $2\text{FeO} \cdot 2\text{SO}_3$ and $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3$. From this it appears that 1 atom of oxygen will oxidize 2FeO to Fe_2O_3 , or 2 molecules of ferrous sulphate to 1 molecule of ferric sulphate, the additional quantity of SO_3 being supplied by 1 molecule of sulphuric acid, that is,

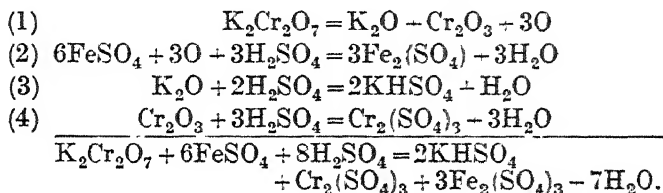


and 5O will oxidize 10FeSO_4 , so the equation is obtained,



This is equivalent to equations 2 and 3 above.

Example. Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, is reduced by ferrous sulphate, in the presence of sulphuric acid. The products are potassium hydrogen sulphate, chromic sulphate, $\text{Cr}_2(\text{SO}_4)_3$, ferric sulphate and water. Divide potassium dichromate into its oxides, write the partial equations as in the last example, and add together. One molecule of potassium dichromate gives 3 atoms of available oxygen.



From these two examples we realize the necessity for the presence of sulphuric acid when potassium permanganate and potassium dichromate are reduced by ferrous sulphate. It is required to convert the potassium oxide and the oxides of manganese and chromium into sulphates. The last two oxides are insoluble in water, and would interfere with the reaction unless they were changed into soluble sulphates.

Additional Examples

Example. Dilute nitric acid acts on tin, giving stannous nitrate, $\text{Sn}(\text{NO}_3)_2$, ammonium nitrate and water. Write the equation.

Example. Sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$, water and chlorine react, giving sodium sulphate, Na_2SO_4 , sulphuric acid and hydrochloric acid. Write the equation.

Example. Sulphur dioxide, SO_2 , reduces potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, giving potassium sulphate, K_2SO_4 , chromic sulphate $\text{Cr}_2(\text{SO}_4)_3$, sulphuric acid and water. Balance the equation.

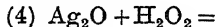
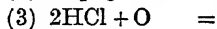
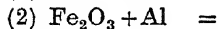
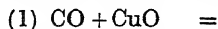
Example. The action of concentrated hydrochloric acid on potassium dichromate gives potassium chloride, KCl , chromic chloride, CrCl_3 , water and chlorine. Balance the equation.

Example. A solution of sodium aluminate, NaAlO_2 , when acted upon by carbon dioxide gives sodium carbonate, Na_2CO_3 , and aluminium hydroxide, $\text{Al}(\text{OH})_3$. Balance the equation.

Example. Calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, sand or silica, SiO_2 , and carbon when heated together, give calcium silicate, CaSiO_3 , carbon monoxide and phosphorus, P. Write the equation.

QUESTIONS

1. Complete the following equations, making such changes in the numerical proportions as you consider necessary.



The above equations represent oxidizing and reducing actions. Indicate the oxidizing and reducing agent in each case.

(Scot. Univ. Entrance.)

CHAPTER XXVI

THE HALOGENS. FLUORINE. CHLORINE

THE name **Halogen** is derived from the Greek word *hals*, meaning 'sea salt,' and signifies 'salt producer,' or 'salt generator.' It is applied to a family of four elements, fluorine, chlorine, bromine, and iodine, because they unite with sodium to form salts resembling common salt. These four show a close relationship in chemical and physical properties, and there are many such groups among the elements. Some examples are :

Helium.	Lithium.	Calcium.	Nitrogen.
Neon.	Sodium.	Strontium.	Phosphorus.
Argon.	Potassium.	Barium.	Arsenic.

The following table shews some of the physical and chemical properties of the halogen family.

	Fluorine.	Chlorine	Bromine.	Iodine
Atomic weight -	19	35.5	80	127
State -	gas	gas	liquid	solid
Colour of vapour	yellow	greenish yellow	brown	violet
Boiling point -	-187°	-34°	60°	183°
Unites with hydrogen	rapidly without a light	rapidly in strong light	rapidly when heated	slowly even when heated

The halogens are all non-metallic monovalent elements and unite with hydrogen to form acids, hydrofluoric acid, HF, hydrochloric acid, HCl, hydrobromic acid, HBr, and hydriodic acid, HI.

It will be observed from the table that there is a gradual transition of physical properties from fluorine to iodine. Their

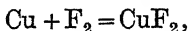
chemical activity decreases in the same order. Fluorine can displace chlorine from chlorides, bromine from bromides, iodine from iodides. Chlorine can displace bromine and iodine, and bromine can displace iodine.

Fluorine

Fluorine. Symbol F. Atomic weight, 19.

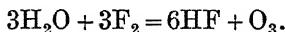
Occurrence. Many minerals contain fluorine in combination with metals as fluorides. Chief of these are calcium fluoride, CaF_2 , also known as *fluorite* or *fluorspar*. An important mineral is *cryolite*, $\text{AlF}_3 \cdot 3\text{NaF}$, used in the manufacture of aluminium.

Preparation of Fluorine. This is a difficult operation, as the compounds of fluorine are very stable and hard to decompose, and the chemical activity of the gas is so great that it destroys the vessel in which it is contained. H. Moissan (1886) was the first to isolate the element. It was discovered that a copper vessel can be used to contain fluorine. At first it attacks the copper vigorously, uniting with it to form copper fluoride,

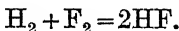


but soon a crust of this substance forms on the surface of the copper which protects it from further action. The gas is obtained by the electrolysis of liquefied hydrofluoric acid, to which potassium fluoride is added to make it conducting.

Properties. Fluorine is a yellow gas. It is the most chemically active element known. It attacks and combines with almost all the metallic and non-metallic elements, usually with flame or explosion, but does not unite with oxygen, chlorine or nitrogen. It decomposes water, giving hydrogen fluoride and ozone.

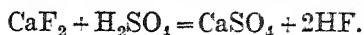


Hydrogen Fluoride, or hydrofluoric acid, HF, is the most important compound of fluorine. When hydrogen and fluorine are brought together, they combine with explosion, giving hydrogen fluoride,



Preparation of Hydrogen Fluoride. The acid is usually prepared by warming powdered fluorspar with concentrated sul-

phuric acid in a retort of platinum or lead, and absorbing the gaseous hydrogen fluoride in leaden vessels containing water.



A solution of hydrogen fluoride or hydrofluoric acid dissolves most metals; the noble metals, platinum, gold, and silver, are not affected, and some become covered with a protecting film of fluoride. It also attacks glass, and is therefore kept in bottles made of wax or rubber.

Uses of Hydrofluoric Acid. Glass may be etched with the gas or its solution in water.

EXPT.—Take a clock glass and brush over its convex surface with melted paraffin wax. When cold, write upon the waxed surface with a metallic point. Put a little powdered fluor-spar and concentrated sulphuric acid into a small basin made from a piece of sheet lead. Cover the basin with the clock glass waxed side down, and heat gently. In a short time the writing will be etched into the glass. The wax is then melted off or washed off with turpentine.

Hydrofluoric acid is used for making the scales on graduated glass instruments, and for cleaning the outside of granite or other stone buildings.

Fluorides. Hydrofluoric acid acts upon metals, oxides, hydroxides and carbonates, giving salts known as fluorides. Most of the fluorides are soluble in water.

Chlorine

Chlorine. Symbol Cl, atomic weight 35.5.

Occurrence. Chlorine is not found free in nature. In combination it is found in common salt, sodium chloride, NaCl. Two-thirds of the solids in sea water consist of common salt, and in Cheshire in England, in Spain, in Germany, and in other countries, great underground beds of salt exist which have been probably formed by the evaporation of sea water in past ages.

History. Scheele (1774) found that a greenish yellow gas is produced when manganese dioxide and hydrochloric acid are heated together. This he called 'dephlogisticated muriatic acid'—that is, muriatic acid (the old name for hydrochloric acid) which has been deprived of phlogiston. Lavoisier (1789) considered it to be an oxide of hydrochloric acid and called it

oxymuriatic acid. Davy (1810) tried to decompose the gas by various methods, but in vain. He therefore concluded that it was an element and gave it the name Chlorine, from the Greek *chloros*, 'green,' on account of its colour.

Preparation. Scheele's method is generally used in the laboratory to prepare the gas.

EXPT.—To prepare chlorine and observe its properties. Fit up the apparatus as shown. Take about 30 grams of manganese

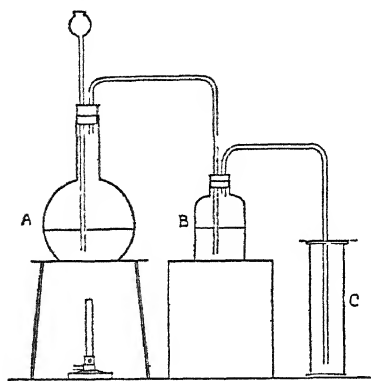


FIG 82.

dioxide, moisten it with water and place it in flask *A*, which is fitted with thistle funnel and delivery tube, and connect up. Add sufficient strong hydrochloric acid to cover the manganese dioxide and warm gently. The chlorine given off is passed through water in the washing bottle, *B*, to free it from hydrochloric acid gas. It is collected by downward displacement in jar *C*, which is covered with a piece of cardboard having a hole in the centre to admit the tube. The experiment is best performed in a fume chamber. Collect half a dozen jars of the gas,

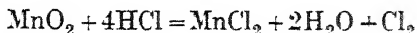
cover them with glass plates, and apply the following tests.

1. Note the greenish yellow colour and irritating smell, but avoid breathing the gas. Test it with starch iodide paper.
2. Throw a small quantity of powdered antimony into a jar.
3. Introduce a small piece of phosphorus in a deflagrating spoon.
4. Moisten a piece of filter paper with warm turpentine and drop it into a jar.
5. Test the gas with a burning taper or candle.
6. Place in a jar a well-dried piece of each of the following : litmus paper, ordinary paper written upon with ink, red flannel. Cover with a plate.
7. At the same time place another set of pieces, previously moistened with water, in another jar. Cover with a plate. Note any changes, and observe which set changes first.

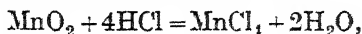
Observe carefully any changes which take place in these

experiments, make notes, and compare them with the explanations which will be given later.

The equation representing the preparation of chlorine by this method is :



The metal manganese has a variable valency. In MnO_2 its valency is 4, $\text{O}=\text{Mn}=\text{O}$. Manganese dioxide is not a basic oxide: the most stable salts of manganese are those corresponding to the oxide MnO , in which the metal is divalent. We may then suppose that the first action is,



and the MnCl_4 , being unstable, breaks up :



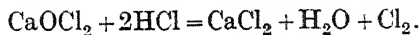
This reaction is really an oxidizing one. the oxidation of hydrochloric acid, the motive being the attraction of oxygen for hydrogen to form water. Hydrochloric acid is therefore a reducing agent, and we may expect that some other oxidizing agents will liberate chlorine from hydrochloric acid.

EXPT.—Try the effect of some oxidizing agents on hydrochloric acid. Warm a small quantity of each of the following substances in a test tube with strong hydrochloric acid: red lead, Pb_3O_4 , litharge, PbO , potassium permanganate, KMnO_4 , copper oxide, CuO , potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, potassium chlorate, KClO_3 . Which of these liberate chlorine from hydrochloric acid?

A convenient method of obtaining chlorine is the use of potassium permanganate as the oxidizing agent.

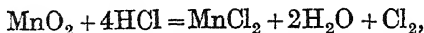
EXPT.—Fit up a flask with a dropping funnel and delivery tube. Place in the flask some potassium permanganate crystals and run in drop by drop a mixture of concentrated hydrochloric acid with an equal bulk of water. The gas may be collected by downward displacement. It is fairly soluble in cold water, and attacks mercury, so that these liquids are not suitable for use in the pneumatic trough. It may, however, be collected over warm water which has been saturated with common salt, in which it is less soluble.

A third laboratory method makes use of Kipp's apparatus, charged with cubes of bleaching powder, CaOCl_2 , and hydrochloric acid.

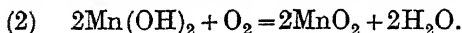
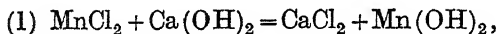


Commercial Processes for the Manufacture of Chlorine

1. The Weldon Process. Chlorine was formerly made commercially by the laboratory method already given, the oxidation of hydrochloric acid by manganese dioxide. On examination of the reaction,



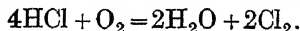
we see that the manganese is transformed into manganous chloride, which has no value, and is therefore a waste product. Such losses must be avoided as far as possible in commercial processes, as they increase the expense of production, so the Utilisation of By-products is a matter of great importance in industrial chemistry. In order to make the manganese again available for oxidation, the Weldon recovery process is employed. The liquid containing manganese chloride is mixed with milk of lime—that is, lime shaken up with water and containing calcium hydroxide, $\text{Ca}(\text{OH})_2$. Air is then blown through the mixture. The action may be divided into two stages.



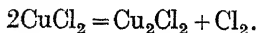
The resulting manganese dioxide, known as 'Weldon's mud', is really a compound with lime, but can be used again to supply oxygen. This process is now in disuse.

2. Deacon's Process, another commercial method used still to some extent, employs atmospheric oxygen as the oxidizing agent, helped by that useful servant of chemistry, a catalyst.

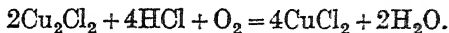
When a mixture of oxygen and hydrochloric acid gas is heated these substances interact slowly, producing chlorine and water. The speed of the reaction is greatly increased by the use of cupric chloride, CuCl_2 , as a catalyst.



The process is as follows. Lumps of pumice are saturated with cupric chloride solution and placed in a tube. The pumice is heated to 350° and a mixture of air and hydrogen chloride is passed through the tube. The cupric chloride is decomposed into cuprous chloride and chlorine,



A reaction then takes place between the cuprous chloride, the hydrogen chloride and oxygen. There is a double pull upon the hydrogen chloride, the cuprous chloride desires more chlorine to form cupric chloride, the oxygen attracts the hydrogen to form water. The result may be expressed in the equation,



The re-formed cupric chloride breaks up again into cuprous chloride and chlorine, so the process is continuous. The chlorine is, of course, largely mixed with nitrogen from the air employed.

3. The Castner-Kellner Process. Most of the chlorine used industrially is now made by the electrolysis of a solution of sodium chloride, sodium hydroxide and hydrogen being obtained at the same time. The Castner-Kellner electrolytic cell consists of a slate tank divided into three compartments by partitions, which dip into grooves in the bottom. On the floor

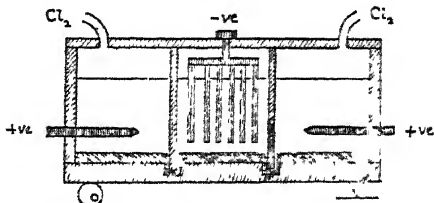


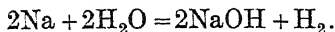
FIG 83.—Castner-Kellner Electrolytic Cell.

of the tank is a layer of mercury, which can flow from end to end under the partitions and acts as a seal to separate the compartments. The two outer compartments contain a strong solution of salt, and also the positive electrodes or anodes, which are of graphite. The inner compartment is partly filled with water and contains an iron grid, which acts as the negative electrode or cathode. By means of an eccentric, the cell can be rocked slowly to keep the mercury circulating along the floor. When the current passes, the sodium chloride is electrolyzed :



The negative chlorine ion goes to the anode, gives up its negative charge and unites with another chlorine atom to form molecular chlorine, Cl_2 , which passes through a pipe in the top of the cell and is collected. The sodium ion travels towards the cathode and enters into the mercury, giving up its positive charge and forming an Amalgam. Mercury forms many com-

pounds with other metals, and these are known as amalgams. The sodium is carried with the mercury into the centre compartment, where it comes in contact with water and reacts with it in the way we already know, giving sodium hydroxide and hydrogen.



Observe that in this process there are no waste products, the three substances obtained, chlorine, sodium hydroxide, and hydrogen, are all commercially valuable. See p. 216

Properties of Chlorine. Chlorine is a greenish yellow gas. It has a disagreeable odour and a very corrosive action on the mouth, throat, and lungs. Irritation caused by inhaling chlorine may be relieved by breathing ammonia. Ammonia and chlorine react together, giving hydrochloric acid and nitrogen. The ammonia then unites with the hydrochloric acid, giving ammonium chloride, a mild and inoffensive substance.

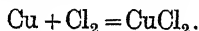
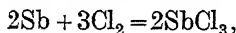
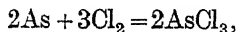


Chlorine is easily liquefied by cold and pressure to an orange yellow liquid, boiling at -33°C . Further cooling transforms it into a yellow solid.

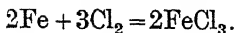
The chemical activity of chlorine is generally greater than that of oxygen, and elements which combine with oxygen to form oxides usually unite with chlorine to form chlorides.

Most metallic and non-metallic elements unite with chlorine directly; exceptions are oxygen, nitrogen, and carbon, whose chlorides are made indirectly.

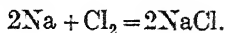
Arsenic, antimony, and copper leaf (known as 'Dutch metal,' and used as a substitute for gold in 'gilding') take fire when dropped into a jar of chlorine. *N.B.*—The fumes of the chlorides of arsenic and antimony are poisonous.



Iron powder burns in chlorine, but requires to be previously warmed.

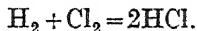


Sodium when heated in a current of chlorine burns brilliantly, giving sodium chloride.



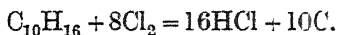
Phosphorus takes fire when introduced into chlorine. The product is a mixture of two chlorides, PCl_3 and PCl_5 , phosphorus trichloride and phosphorus pentachloride.

If a jet of hydrogen is lighted and introduced into a jar of chlorine it burns with a greenish flame, forming hydrogen chloride, which gives white fumes when it comes in contact with moist air.



A mixture of equal volumes of hydrogen and chlorine, when exposed to bright sunlight or ignited with a burning taper, explodes violently, giving hydrogen chloride. The gases do not combine in the dark, but unite slowly in diffused daylight.

The attraction of chlorine for hydrogen is so great that it extracts hydrogen from many compounds. A lighted taper continues to burn in chlorine, giving a black smoke due to small particles of carbon, and a piece of filter paper wetted with warm turpentine takes fire in the gas. The equation for the burning of turpentine is,

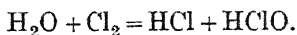


Turpentine is a member of a class of substances known as hydrocarbons, which contain only hydrogen and carbon. When the hydrogen is removed by chlorine, carbon is set free and appears as a black cloud of soot.

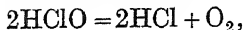
Some metals, such as iron and copper, do not unite with perfectly dry chlorine; indeed there are many chemical reactions which refuse to proceed if the reacting substances are absolutely freed from moisture—in such cases water seems to act as a catalyst.

Chlorine possesses strong oxidizing and bleaching properties, which depend primarily on its attraction for hydrogen. For bleaching we have already found by experiment that the presence of water is necessary.

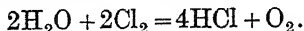
Cold water dissolves about three times its own volume of chlorine, forming the solution known as 'chlorine water.' In this solution a slow reaction takes place, giving hydrochloric acid and hypochlorous acid, HClO .



Hypochlorous acid loses oxygen slowly, giving hydrochloric acid,



and if chlorine water be exposed to sunlight the final products are hydrochloric acid and oxygen.



Chlorine water liberates iodine from potassium iodide solution and bromine from potassium bromide solution.

EXPT.—Take a little potassium iodide solution in a test tube. Add a few drops of chloroform or carbon disulphide and some chlorine water. Shake up. The chloroform collects and dissolves the liberated iodine, showing a violet colour. This is a characteristic test for iodide.

EXPT.—Repeat the last experiment, using potassium bromide. Bromine is set free, giving with the chloroform a brown solution. This is a test for a bromide.

Uses of Chlorine. Chlorine is extensively used in the manufacture of bleaching powder for bleaching cotton, linen, and wood pulp for paper-making. It is also a killer of typhoid and other germs, and is used for purifying water supplies. The quantity added is so small that it has no unpalatable or injurious effect, and the cost is about one shilling per million gallons of water treated.

During the Great War (1914-18) a new destructive weapon, the gas attack, was invented. The first gas used was chlorine, which was released from cylinders of liquid chlorine in the trenches, when there was a favourable wind to carry it into the enemy lines. The density of chlorine is $2\frac{1}{2}$ times that of air, so the greenish cloud rolled along the ground and filled the trenches, rendering the tortured soldiers helpless to resist attack. Later in the War other gases were used by both sides—'tear gas,' 'mustard gas,' etc. It is said that some of these gases were so deadly that one part of the gas in ten million parts of air was sufficient to put a man out of action.

In defence, gas masks worn over the nose and mouth were invented which generally contained powdered charcoal, an excellent gas absorber, as well as chemical substances like soda-lime (a mixture of caustic soda and slaked lime), potassium permanganate and sodium thiosulphate. The direct gas attack was soon abandoned, as occasionally the wind changed during the attack and blew the gas back upon the assailants, and

shells containing volatile liquids which became gasified by the heat of the explosion were afterwards used.

Additional Experiments

EXPT.—Carry out Deacon's process as described.

EXPT.—Produce chlorine, using other dioxides instead of manganese dioxide.

EXPT.—Burn a jet of hydrogen in chlorine and a jet of chlorine in hydrogen. Test for hydrochloric acid with a filter paper wetted with ammonia solution.

EXPT.—Burn sodium in chlorine.

EXPT.—Blow a thin-walled bulb on a piece of soft glass tubing. Soften the tube on each side of the bulb, draw out and cut off. Make a few of these bulbs. Fill them with the products of the electrolysis of concentrated hydrochloric acid. The electrolysis should be allowed to proceed for two hours to saturate the liquid with chlorine before collecting the mixed gases. Seal off the bulb. They may be exploded under a glass shade by the light from burning magnesium ribbon.

QUESTIONS

1. Describe, with a sketch of the apparatus, a laboratory method for preparing chlorine. What impurities would the gas, so prepared, be likely to contain, and how would you get rid of them.

(Oxford and Camb. School Cert.)

2. Mention the investigators whose names are associated with the discovery of hydrogen, oxygen, nitrogen and chlorine. Give such particulars as you know concerning the discovery of any one of these gases.

(Scot. Univ. Entrance)

3. State the conditions for the action (if any) of chlorine on (a) water, (b) sulphuretted hydrogen, (c) copper, (d) phosphorus, (e) potassium iodide, (f) slaked lime. Give equations.

(Oxford and Camb. School Cert.)

4. Mention three elements usually associated with chlorine, and draw up a table comparing the properties of the four elements. Mention two other sets of similarly related elements.

(Scot. Leaving Cert.)

5. How is hydrogen fluoride prepared? By what other name is it known? Mention one of its uses, and describe an experiment illustrating this use.

6. Give an account of two commercial processes for the manufacture of chlorine, including an electrolytic method. What are the chief uses of chlorine?

CHAPTER XXVII

COMMON SALT. HYDROGEN CHLORIDE. HYPOCHLORITES. CHLORATES

Common Salt, or sodium chloride, NaCl , is the raw material from which chlorine and its compounds, as well as sodium and its compounds, are derived.

We have already seen that sea water contains $2\frac{1}{2}\%$ of common salt, and that there are in various countries extensive underground beds of 'rock salt.' These beds may be mined like coal, or water may be poured down a shaft to dissolve the salt and the solution pumped up and evaporated in pans. The slower the evaporation the larger are the crystals of salt.

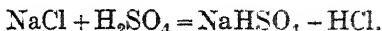
Properties. Sodium chloride is a white substance crystallizing in cubes. Its solubility is nearly as great in cold water as in hot, and the concentrated solution is known as brine. Water and salt, two substances indispensable in our daily lives, are surprising examples of chemical change, and show that the properties of a compound are often very different from those of its constituents. In the former, two very active gases unite to form a very inert liquid, and in the latter, a white silvery metal unites with a green poisonous gas, giving a mild and palatable seasoning for our food.

Uses. Large quantities of salt are used in chemical industry in the manufacture of chlorine, hydrochloric acid, caustic soda, sodium carbonate and soap. It is used in preserving fish, meat, and other foods, and in cooking, as a flavouring and aid to digestion.

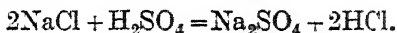
Hydrogen Chloride, or hydrochloric acid, HCl . This important compound is a gas which dissolves readily in water. The solution has strongly acid properties, and was known to the Arabian chemists. Glauber (1658) was the first to describe its preparation from common salt by distillation with concen-

trated sulphuric acid. The white fumes produced he dissolved in water, and the acid solution, on account of its derivation from common salt, was called *Spirit of Salt*. Priestley (1772) investigated the properties of the gas, and found that though soluble in water it could be collected over mercury. He named the acid *Muriatic Acid*, from the Latin *muria*, meaning 'brine.'

Preparation. Hydrogen chloride can be made by the action of concentrated sulphuric acid on many chlorides, but sodium chloride is usually employed. The equation for the action of sulphuric acid on sodium chloride, using diluted acid and a low temperature is :



Acid sodium sulphate or sodium bisulphate is produced. Using concentrated acid and a high temperature, the normal salt is obtained.



EXPT.—To make hydrogen chloride. Fit up a flask with thistle funnel and delivery tube as shown. In the generating flask place some sodium chloride and cover it with a mixture of 2 parts of concentrated sulphuric acid and 1 part of water, pouring the acid slowly into the water as usual. The gas is dried by passing it through concentrated sulphuric acid in the second flask and collected in jars by downward displacement. Warm, and collect two or three jars of the gas. Finally put a little water into a jar and pass the gas through it for a few minutes.

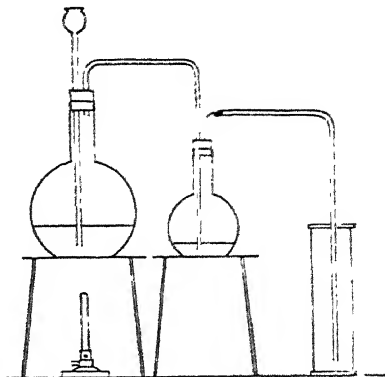


FIG 84

Upward or Downward Displacement. A warning may be given here with regard to the use of these terms. We have been using them in the sense that a gas lighter than air goes upward, and a gas heavier than air goes downward. In some books, however, they have just the opposite meaning. Hydrogen goes upward, but it displaces the air in a vessel downwards, and is

therefore said to be collected by downward displacement of air. Carbon dioxide, a heavy gas, goes downward, but the air which it displaces goes upward, so it is said to be collected by upward displacement of air. In answering examination questions it is wise to state exactly what you mean by upward and downward displacement.

EXPT.—To find out some of the properties of hydrogen chloride

1. Observe the irritating odour of the gas and the white fumes which appear when it meets moist air. A cloud of minute drops of hydrochloric acid solution is formed.

2. Test its acid reaction with a piece of moist blue litmus paper.

3. Find out whether it is combustible or a supporter of combustion, by introducing a burning taper into the gas. Also try whether such substances as sulphur, phosphorus, sodium and magnesium, which burn in oxygen, will also burn in hydrogen chloride.

4. Moisten a piece of filter paper with ammonia and hold it in the gas.

5. Test with litmus paper the water through which the gas has been passed. Has it dissolved any hydrogen chloride? Try its effect on zinc, iron, and magnesium in a test tube. Has it any action on carbonates? Do its properties resemble those of dilute hydrochloric acid?

A convenient way of obtaining a steady stream of hydrogen chloride is to run concentrated sulphuric acid drop by drop from a dropping funnel into a flask containing concentrated hydrochloric acid.

Commercial Preparation of Hydrochloric Acid

1. The bulk of the hydrochloric acid used commercially is made by the 'saltcake' process. Half a ton of coarse salt is heated with its own weight of concentrated sulphuric acid in a cast-iron pan. Sodium bisulphate is first produced, but on final heating to redness this is converted into the normal sulphate, known as 'saltcake.' The hydrogen chloride is passed into towers packed with coke, kept wet by running water which absorbs the gas. A solution of hydrochloric acid containing about 35% of HCl is finally obtained.

2. We have seen that in the Castner-Kellner process for the electrolysis of sodium chloride, two of the products are hydrogen and chlorine. A considerable quantity of hydrochloric acid is now made by uniting these by combustion and

absorbing the resulting hydrogen chloride in water. This process gives a very pure acid.

Properties of Hydrogen Chloride. Hydrogen chloride is a colourless gas, giving white fumes when it comes in contact with moist air. It has a pungent smell, but is not poisonous. It can be condensed into a liquid boiling at -85° . Dry hydrogen chloride gas has no action on litmus paper, and liquid hydrogen chloride has no action upon some metals and carbonates which dissolve readily in hydrochloric acid. Water dissolves at 15° 455 times its own volume of hydrogen chloride. The solubility of the gas may be shown by the fountain experiment.

EXPT.—Take a half-litre round-bottom flask and fit it with a one-hole rubber stopper through which passes a piece of glass tube. The end of the tube inside the flask is drawn out to a jet, and the other end has attached to it a couple of inches of rubber tubing carrying a clip. The flask is filled with hydrogen chloride by downward displacement and the stopper and tube replaced, the clip being closed. Support the flask on a retort stand, with the rubber tubing dipping into water as shown. The water should be coloured with purple litmus. Open the clip under water. If the water does not rise in the tube quickly, warm the flask gently to expel a few bubbles of gas. When the flask cools the water rises, the hydrogen chloride dissolves in it, forming a partial vacuum, and the outside pressure forces up the water into the flask in the form of a fountain. The litmus is reddened by the acid solution. The arrangement in Fig. 72 may be used if preferred.

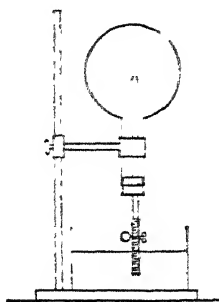
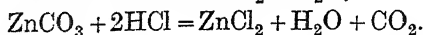
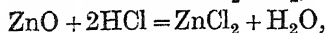
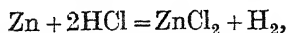


FIG. 85—Hydrogen Chloride Fountain

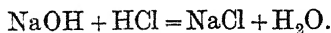
Ordinary concentrated hydrochloric acid contains about 35% of the substance HCl . If this solution is distilled, hydrogen chloride is driven off till the strength of the remaining acid is 20%, and this acid then passes over unchanged. If a solution weaker than 20% is distilled, water passes over until the strength of the acid is 20%, when it begins to distil unchanged. Hydrochloric acid of 20% strength is consequently called 'constant boiling' acid.

Hydrochloric acid dissolves many metals, giving the chloride of the metal and hydrogen. It also dissolves most oxides and

hydroxides, giving the chloride and water. It decomposes carbonates, giving the chloride, carbon dioxide, and water.



It neutralises alkalies, like all acids, giving a chloride and water



Composition of Hydrogen Chloride. The molecule of hydrogen chloride contains hydrogen and chlorine. The presence of hydrogen can be shown by passing the dried gas over heated iron or zinc and collecting the gas given off over water.

EXPT—The apparatus is fitted up as illustrated. *A* is the generating flask containing salt and sulphuric acid. *B* is a drying flask containing concentrated sulphuric acid. *C* is a hard glass tube in which some iron filings or pieces of sheet zinc are placed,

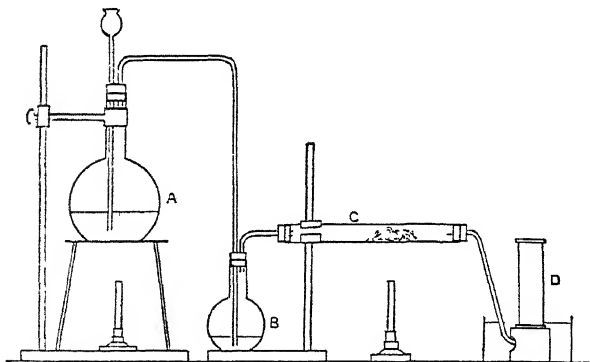


FIG. 86.

and *D* is a jar filled with water standing in a pneumatic trough. *A* is warmed and a current of hydrogen chloride passed till all air is driven out of the apparatus. This point is reached when no more air collects in the jar, *D*. The hydrogen chloride dissolves in the water in the trough. Then fill *D* again with water, replace it, and heat the iron. A gas collects in the jar which may be shown to burn with a blue flame like hydrogen.

Using the same apparatus, but dispensing with the pneumatic trough and jar, we can show that hydrogen chloride contains

chlorine. In this instance, put some manganese dioxide into the tube instead of iron. Pass a current of hydrogen chloride through the tube and heat the dioxide. Test the issuing chlorine by smell, with starch iodide paper and moist litmus paper.

These experiments prove that hydrogen chloride contains hydrogen and chlorine. They do not, however, show the relative proportions of these, neither do they prove that it contains no other elements.

We can take equal volumes of hydrogen and chlorine and combine them to produce hydrogen chloride, and we can decompose hydrochloric acid by electrolysis and show that it contains equal volumes of hydrogen and chlorine.

Synthesis of Hydrogen Chloride. This may be carried out in a glass tube of the shape illustrated. It consists of two bulbs of equal size with three stopcocks. The middle one, *D*, is a three-way tap, and can be set in 5 different positions.



FIG. 87.

1. *A* and *B* can be connected.
2. *A* can be connected with air through *D*.
3. *B* can be connected with air.
4. Both *A* and *B* can be connected with air and with each other.
5. *A* and *B* can be disconnected from each other and from air.

Try to draw a diagram of such a tap.

First open tap *C* and set tap *D* in position 2. Then fill *A* with chlorine. Close tap *C*, set tap *D* in position 3, open tap *E* and fill *B* with hydrogen. Then close *E* and set tap *D* in position 1. Allow the gases to mix for a few hours exposed to diffused daylight. When the greenish colour of chlorine has entirely disappeared, open tap *C* under mercury. If no gas escapes and no mercury enters the tube, there has been no change of volume. Then close *C* and open it again under water, the water will rise and fill the tube. Pour the solution of hydrochloric acid into a beaker and apply some of the tests already given.

One volume of chlorine unites with one volume of hydrogen to form two volumes of hydrogen chloride, so that there is no change of volume on combination. The vapour density of hydrogen chloride is 18.25. From these data derive the formula by the method already given.

Electrolysis of Hydrochloric Acid. An apparatus as illustrated is used. The tubes are filled with concentrated hydrochloric acid,

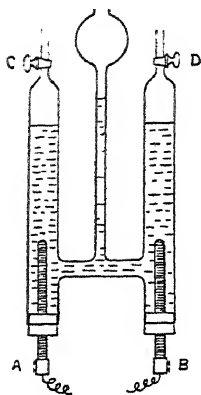


FIG. 88.

which has been saturated with sodium chloride to lessen its power of dissolving chlorine. The electrodes *A* and *B* are made of carbon, as chlorine attacks metals. When the current is passed it will be observed that the volume of hydrogen is greater than the volume of chlorine as some chlorine dissolves in the liquid. The current must therefore be passed with the taps *C* and *D* open until the liquid is saturated. The tubes are then filled with acid, the taps closed and the electrolysis proceeded with. The volumes of hydrogen and chlorine should now be equal. The hydrogen which comes off at the cathode may be tested with a light, and the chlorine coming off at the anode may be tested with starch iodide paper.

It can be proved by analysis that the quantity of hydrogen chloride in solution has decreased, and that the decrease is equal to the weight of chlorine and hydrogen evolved.

In what respects and why does the electrolysis of concentrated hydrochloric acid differ from the electrolysis of dilute sulphuric acid as already explained?

Uses of Hydrochloric Acid. Its chief use is in the manufacture of chlorine. It is also used for cleaning iron before plating with zinc or tin, and in making metallic chlorides.

Chlorides. Chlorine unites with other elements to form chlorides. The following are methods of making chlorides, with some of which we are already familiar.

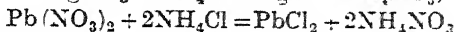
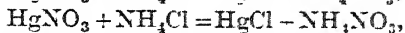
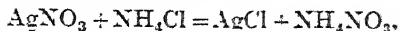
1. Heating a metal or non-metal in chlorine; some, as we have seen, combine without heating. This gives the anhydrous chloride.

2. The action of hydrochloric acid on a metal, a basic oxide, a hydroxide, or a carbonate. The chloride is obtained by evaporation and crystallization of the solution.

3. Chlorides which are insoluble in water can be prepared by precipitation. There are three insoluble chlorides: silver chloride, AgCl , mercurous chloride, HgCl and lead chloride, PbCl_2 .

EXPT.—Take solutions of silver nitrate, AgNO_3 , mercurous nitrate, HgNO_3 , and lead nitrate, $\text{Pb}(\text{NO}_3)_2$, in test tubes, and add

to each a little ammonium chloride solution. A white precipitate of the chloride is obtained in each case.



The empirical or simplest formula of mercurous chloride is HgCl , but it is frequently written Hg_2Cl_2 for vapour density reasons. The chlorides of all the other common metals are soluble in water.

Tests for Chlorides

1. Add to the solution silver nitrate, a white precipitate soluble in ammonia solution indicates the presence of chloride.

2. Heat a few crystals of a chloride in a test tube with concentrated sulphuric acid; hydrogen chloride is given off.

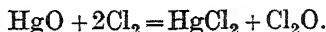
3. On heating a chloride with manganese dioxide and sulphuric acid, chlorine is evolved.

EXPT.—Take a little sodium chloride, NaCl , in a test tube and add strong sulphuric acid. Heat, note the smell, and test with moist blue litmus paper.

EXPT.—Heat some copper chloride, CuCl_2 , with manganese dioxide and strong sulphuric acid and test for chlorine.

Oxides of Chlorine. Chlorine forms two oxides, chlorine monoxide, Cl_2O , and chlorine peroxide, ClO_2 . They are both unstable and highly explosive compounds.

The monoxide is prepared by passing chlorine gas over mercuric oxide. The mercuric oxide is precipitated and heated beforehand to coarsen the grain and slow down the speed of reaction :



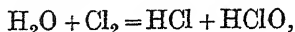
Chlorine monoxide is a reddish yellow gas which dissolves in water, giving hypochlorous acid.

Chlorine peroxide or dioxide, ClO_2 , is made by adding powdered potassium chlorate to concentrated sulphuric acid. The oxide is given off as a heavy, yellow, and very explosive gas, and is a powerful oxidizing agent.

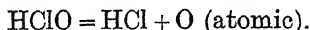
EXPT.—Place a small crystal of potassium chlorate on a block of wood and touch it with a glass rod carrying a drop of concentrated sulphuric acid.

EXPT.—Burning phosphorus under water. Place a few crystals of potassium chlorate and one or two small pieces of phosphorus in a glass of water. Introduce a thistle funnel into the glass and pour down a little strong sulphuric acid. Chlorine peroxide is formed, which oxidizes the phosphorus, giving flashes of light.

Hypochlorous Acid. We have seen that chlorine acts slowly upon water, giving hydrochloric acid and hypochlorous acid,



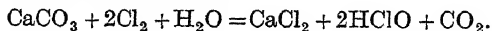
and that if chlorine water is exposed to bright sunlight the hypochlorous acid also decomposes, giving hydrochloric acid and oxygen,



EXPT.—Fill a long tube with chlorine water and invert it with the lower end dipping into water in a basin. Allow it to stand in bright sunlight. A gas is evolved which supports the combustion of a glowing wood splinter.

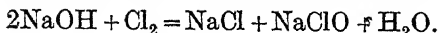
Hypochlorous acid is a powerful oxidizing and Bleaching agent. These properties are due to the readiness with which it gives up oxygen. Molecular oxygen, O_2 , is not a bleacher, but when oxygen is formed in the atomic or 'nascent' state in a reaction, it is much more active than it is after the atoms have united with each other to form molecules. The bleaching action of chlorine and chlorine water is due to the presence of hypochlorous acid.

EXPT.—To make a solution of hypochlorous acid. Shake up powdered calcium carbonate with cold water in a flask, and pass a stream of chlorine through it, shaking occasionally. Filter to remove the remaining carbonate. The filtrate contains calcium chloride and hypochlorous acid.



Test the bleaching action of this solution on litmus paper, indigo, coloured flowers, turkey red cloth.

Action of Chlorine on Alkalies. If a stream of chlorine is passed through caustic soda solution, sodium hypochlorite and sodium chloride are formed. The liquid should be kept cold.

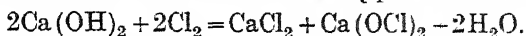


Compare this reaction with the action of chlorine on water, taking the formula of water as HOH.

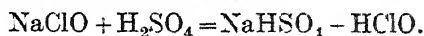
Caustic potash gives a solution of the corresponding potassium salts,

$$2\text{KOH} + \text{Cl}_2 = \text{KCl} + \text{KClO} + \text{H}_2\text{O}.$$

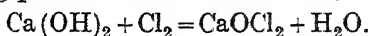
When chlorine is passed through milk of lime, a solution containing calcium chloride and calcium hypochlorite is obtained.



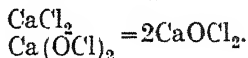
The hypochlorites are salts of hypochlorous acid. They have no bleaching properties until the hypochlorous acid is set free by addition of a dilute acid.



Bleaching Powder is a white powdery substance smelling like chlorine. It has the formula CaOCl_2 , and is made by passing chlorine over dry slaked lime. The chlorine is readily absorbed, giving bleaching powder or chloride of lime,



A solution of bleaching powder in water acts as if it contained calcium chloride and calcium hypochlorite, and the bleaching action is due to the latter, from which hypochlorous acid is set free by a dilute acid. Bleaching powder may be regarded as a double salt,



The formulae of hypochlorous acid and the hypochlorites are frequently written HOCl , NaOCl , $\text{Ca}(\text{OCl})_2$, to correspond with the graphic formula $\text{H}-\text{O}-\text{Cl}$.

Bleaching is a very important industry. Unbleached linen and cotton have a yellow colour, due to a natural brown colouring matter. To whiten it, the material is washed, dipped in bleaching powder solution and afterwards in dilute sulphuric acid. It is again washed, and the last traces of hypochlorous acid and chlorine, which would, if left, rot the fabric, are removed by dipping in an *antichlor*, usually a solution of sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$, the substance known to photographers as 'hypo.' The name 'antichlor' explains itself. Wool and silk are injured by hypochlorous acid, so they are bleached by sulphurous acid. Large quantities of wood, ground to pulp, are used in the manufacture of paper and bleached by bleaching powder. Under the name of 'chloride of lime' it is also used as a disinfectant. When exposed to the air it liberates hypochlorous acid, which destroys harmful germs in the atmosphere by oxidation.

Chlorates. When chlorine is passed through strong potassium hydroxide solution, potassium hypochlorite is first formed. If the stream of chlorine is continued the potassium hypochlorite is transformed into potassium chlorate, with evolution of heat, and crystals of this substance separate from the liquid. The same result is obtained more quickly by passing the gas into hot caustic potash.



The complete reaction is,



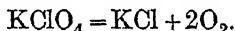
Some other chlorates are sodium chlorate, NaClO_3 , calcium chlorate, $\text{Ca}(\text{ClO}_3)_2$, barium chlorate, $\text{Ba}(\text{ClO}_3)_2$.

The chlorates are white crystalline salts soluble in water. Like potassium chlorate, they are all good oxidizing agents, and are used in match-making and in the manufacture of fireworks. The chlorates are salts of chloric acid, HClO_3 .

Perchlorates. When potassium chlorate is heated, the first change is the formation of potassium perchlorate, KClO_4 .



On stronger heating the perchlorate decomposes again,



The perchlorates are salts of perchloric acid, HClO_4 .

Additional Experiments

EXPT.—Place a crystal of potassium chlorate in a crucible inside a beaker. Add a drop or two of concentrated sulphuric acid. Observe the chlorine peroxide collect in the beaker. Take a long glass rod bent at the end to a right angle, warm the end in the Bunsen flame and explode the gas. Use a *small* beaker and perform the experiment carefully.

EXPT.—Prepare bleaching powder. Support a layer of dry slaked lime on glass wool or asbestos in a filter funnel and pass a current of chlorine through the stem of the funnel for half an hour. Treat with water and filter. Use the solution for bleaching tests with and without the addition of acid.

EXPT.—Prepare potassium chlorate. Pass chlorine through a hot concentrated solution of caustic potash, till it smells strongly of the gas. The gas should be cleaned from hydrochloric acid by washing in water, and enter the potash through an inverted funnel

to prevent choking the outlet tube with crystals. Evaporate further if necessary, cool and drain off the liquid from the crystals. Dissolve them in a little hot water and recrystallize till free from chloride. A crystal dissolved in water should give no precipitate with silver nitrate. Apply tests.

EXPT.—Place some potassium chlorate crystals in a test tube. Add a little hydrochloric acid and warm. A mixture of chlorine and chlorine peroxide is evolved known as *euchlorine*, a greenish yellow gas.

EXPT.—Powder some potassium chlorate and some sugar *separately*. Mix them with a spatula lightly and carefully. Place on an iron or asbestos sheet and add a drop of concentrated sulphuric acid at the end of a glass rod. Vary the experiment by using other chlorates.

QUESTIONS

1. Describe what you would observe when a solution of common salt is (a) heated to drive off the water, (b) treated with silver nitrate solution, (c) heated with sulphuric acid.

(Oxford and Camb. School Cert.)

2. Describe the laboratory method of preparing dry hydrogen chloride. Give a list of its four principal physical, and its three principal chemical properties. Indicate how you would demonstrate two of its chemical properties. How would you show experimentally: (a) that the gas contains hydrogen and chlorine, (b) that the gas contains *only* hydrogen and chlorine.

(Scot. Leaving Cert.)

3. Describe and explain the action of chlorine on (a) metallic sodium, (b) sodium hydroxide solution, and (c) potassium iodide solution.

(London Matric.)

4. How would you prepare from potassium chlorate specimens of the two gaseous elements it contains? One of these gases has a distinct colour and smell. How would you identify the presence of this gas otherwise than by colour or smell? What are its main properties?

(Scot. Univ. Entrance.)

5. Why should one not use strong nitric acid when asked to prepare hydrochloric acid from common salt? How is this gas usually prepared, and what are its properties? What result would you expect to get had nitric acid been used?

(Scot. Univ. Entrance.)

6. How would you prepare a specimen of bleaching powder? Explain its bleaching action. This powder is used as a disinfectant by merely sprinkling it about. How do you explain its action chemically in this case?

CHAPTER XXVIII

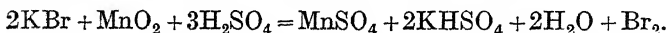
BROMINE AND IODINE

Bromine

Bromine. Symbol Br. Atomic weight 80.

Occurrence. It is not found free in nature. At Stassfurt in Saxony there are great salt beds containing, besides common salt, salts of potassium, magnesium, and calcium. On these deposits the world depends for a large proportion of the supply of potassium salts. They also contain magnesium bromide in small quantities. Most of the bromine of commerce is derived from this source and from mineral springs in Germany and America. Sea water also contains a little magnesium bromide, which is left in the mother liquor after the sodium chloride has been crystallized out by evaporation. Balard (1826) obtained the element from this residue and called it **Bromine**, from a Greek word *bromos*, meaning 'a bad smell.'

Preparation. Chlorine is most readily prepared from hydrochloric acid and manganese dioxide, but it can also be made by warming a mixture of common salt and manganese dioxide with strong sulphuric acid. The salt and the sulphuric acid produce hydrochloric acid, which acts on the manganese dioxide, giving chlorine. The same method is used in preparing bromine, substituting a bromide for the chloride.



A mixture of 3 parts of potassium bromide and 1 part of manganese dioxide is placed in a retort, covered with sulphuric acid, 1 part of acid to 2 parts of water, and distilled. The bromine condenses in a cooled receiver as a dark red liquid.

Commercial Preparation of Bromine. Chlorine displaces bromine from bromides, and this reaction is made use of in the commercial extraction of bromine from salt solutions containing bromide. The salt solution is allowed to trickle down a

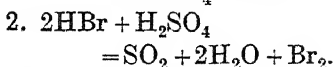
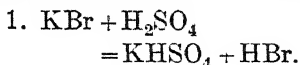
tower packed with earthenware balls. Steam and chlorine are blown in at the base of the tower. Bromine is set free by the chlorine and volatilized by the heat of the steam, passing from the top of the tower into condensers.

EXPT.—Warm a little potassium bromide and manganese dioxide mixture with sulphuric acid in a test tube. Note the colour and smell of the gas evolved.

EXPT.—Dissolve a crystal or two of potassium bromide in water in a test tube, and add chlorine water. Observe the change of colour. Add a few drops of carbon disulphide and shake.

Properties of Bromine. It is a heavy, dark red liquid, giving off an irritating and poisonous vapour. It is an oxidizing agent, with feeble bleaching properties, and is less chemically active than chlorine. Powdered antimony and phosphorus combine with it with a violent reaction. Bromine displaces iodine from iodides.

Hydrogen Bromide or Hydrobromic Acid, HBr. Hydrogen and bromine do not combine when exposed to bright sunlight. When a mixture of the gases, made by passing hydrogen through liquid bromine, is passed through a tube containing a platinum spiral, electrically heated to a red heat, hydrogen bromide is formed. The platinum acts as a catalyst. Hydrogen bromide cannot be made pure by the method used in making hydrogen chloride. If a bromide is warmed with sulphuric acid, a mixture of bromine vapour and hydrogen bromide is obtained. The sulphuric acid oxidizes part of the hydrogen bromide to bromine.



Preparation of Hydrogen Bromide. It is most conveniently made by the action of bromine on phosphorus. Bromine combines with yellow phosphorus explosively, so red phosphorus, the less active allotropic form, is used. Red phosphorus is mixed with sand (to slow down the reaction) and water. The mixture is

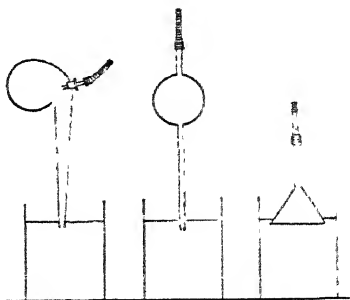
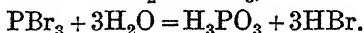
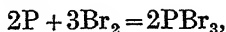


FIG. 89.—Absorption Methods

placed in a flask and bromine added from a tap funnel. On gentle warming hydrogen bromide is given off, which may be freed from bromine vapour by passing through a U-tube containing red phosphorus. The gas may be collected by downward displacement, or passed through water. If the latter method is employed, precautions must be taken against water sucking back owing to the great solubility of hydrogen bromide. A retort may be used, a pipette with a large bulb or a filter funnel just dipping into the water. The bromine and phosphorus combine, forming phosphorus bromide, PBr_3 , and the bromide is hydrolyzed by water, giving phosphorous acid and hydrobromic acid.



Properties of Hydrogen Bromide. These are very similar to the properties of hydrogen chloride. It is a colourless gas, fuming in contact with air. It is more soluble in water than hydrogen chloride. The solution has strong acid properties and dissolves many metals with evolution of hydrogen, giving bromides.

Bromides. These are soluble in water with the exceptions of silver bromide, AgBr , mercurous bromide, HgBr , and lead bromide, PbBr_2 . Potassium bromide is the best known and is used as a sedative in medicine.

Tests for Bromide

1. On heating with concentrated sulphuric acid a brown vapour is given off.
2. The addition of chlorine water to a solution of a bromide gives a brown coloration.
3. Silver nitrate gives a light yellow precipitate.

EXPT.—Carry out these tests, using potassium bromide.

Oxides. Bromine forms no oxides. It gives hypobromous acid and bromic acid, HBrO , and HBrO_3 , resembling the corresponding 'oxyacids' of chlorine. Acids which contain oxygen are frequently called 'oxyacids.' The hypobromites are more unstable than the hypochlorites, so when bromine acts on potassium hydroxide, potassium bromate, KBrO_3 , is formed, even when the solution is dilute.

Iodine

Iodinē. Symbol I. Atomic weight 127.

Occurrence. Iodine is present in minute quantities in sea water as iodide. A certain kind of seaweed which grows round our coasts collects iodide as part of its food. This seaweed was formerly burned and the ash, known as 'kelp,' used for the production of iodine. Courtois (1812) found that when kelp is heated with manganese dioxide and sulphuric acid a violet-coloured vapour is given off, which condenses to a blue-black solid. In 1813 the substance was studied by Davy and Gay-Lussac, who found that it was a new element and gave it the name Iodine, from the Greek word, *ioides*, meaning *violet*.

Kelp-burning, which was once a considerable industry, is now almost extinct in Scotland and Ireland, but survives still in Norway and France.

Iodine is now principally obtained from sodium iodate, NaIO_3 , found in Chile saltpetre. These deposits, found in rainless districts in Chile, are the chief natural source of nitrates.

Preparation of Iodine

1. Iodine is prepared in the same way as bromine, by heating sodium or potassium iodide with manganese dioxide and sulphuric acid in a retort. The iodine comes off as a beautiful purple vapour which condenses, not to a liquid, but to a solid, the process known as sublimation. The substance may be purified by repeated sublimation.



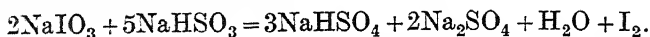
2. The element can also be prepared by passing chlorine through a solution of potassium iodide; iodine is precipitated, as it is not very soluble in water.

Commercial Preparation

1. Kelp obtained by burning seaweed is boiled with water. The solution is concentrated and sodium chloride and other salts crystallize out. The sodium iodide being more soluble, remains in solution. The liquid is then mixed with manganese dioxide and sulphuric acid and distilled, and the iodine is condensed in earthenware receivers. In France the mother

liquor, after crystallization, is treated with chlorine, the iodine is precipitated, filtered off and sublimed.

2. Iodine is obtained from sodium iodate, NaIO_3 , by reduction. The mother liquor, after separation of sodium nitrate from Chile saltpetre, contains sodium iodate. This is treated with sodium bisulphite, NaHSO_3 , which reduces the sodium iodate to free iodine.



The precipitate of iodine is filtered off and purified.

Properties of Iodine. Iodine is a blue-black crystalline solid with a metallic lustre. On warming it gives off a purple vapour of density corresponding to the formula I_2 . It is very slightly soluble in water, but dissolves in alcohol and ether, forming brown solutions, and in carbon disulphide giving a violet solution. With starch it gives a deep blue colour, a very delicate test for free iodine. It combines very slowly with hydrogen, giving hydrogen iodide, HI , but unites readily with phosphorus and many metals, forming iodides.

EXPT.—Test the solubility of iodine in water, alcohol, ether, chloroform and carbon disulphide. Observe the colours of the solutions.

EXPT.—Put a few crystals of iodine into a crucible, and drop in with a tongs a very small piece of phosphorus.

EXPT.—Repeat the experiments in Chap. VI, to make mercurous and mercuric iodides.

EXPT.—Tests for iodine and iodides:

1. Warm a little solid potassium iodide and manganese dioxide in a test tube with sulphuric acid. Observe the colour and smell of the vapour.

2. Add a little of a water solution of iodine to a few c.c. of starch solution in a test tube. Warm the blue liquid and allow it to cool again. Note any changes which take place.

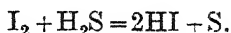
3. Silver nitrate added to a solution of potassium iodide gives a yellow precipitate.

4. Add chlorine water to potassium iodide solution in a test tube; iodine is set free, giving a brown coloration. Add a few drops of carbon disulphide and shake. The carbon disulphide dissolves the iodine, showing a violet colour.

Hydrogen Iodide or Hydriodic Acid, HI . The method of preparing hydrogen iodide is similar to that for preparing

hydrogen bromide, the action of iodine on red phosphorus in the presence of water. The iodine and phosphorus are mixed in a flask and water is slowly dropped in from a dropping funnel. The action is a brisk one. Hydrogen iodide cannot be obtained pure by warming potassium iodide with sulphuric acid as iodine is formed.

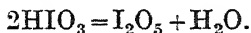
A solution of hydriodic acid can be made by passing hydrogen sulphide gas through water holding iodine in suspension, and filtering off the precipitated sulphur



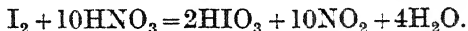
Properties of Hydrogen Iodide. It is a colourless gas, fuming in moist air. It is more easily decomposed by heat than hydrogen chloride and bromide, which it resembles closely in its properties. It is very soluble in water, giving a strongly acid solution of hydriodic acid.

Iodides. These are made like chlorides or bromides. When heated with concentrated sulphuric acid with or without manganese dioxide they give iodine. Chlorine water sets free iodine from a solution of an iodide, and silver nitrate gives a yellow precipitate.

Oxides. Iodine forms two oxides, IO_2 and I_2O_5 . The principal oxide, I_2O_5 , is a white crystalline solid made by heating iodic acid, HIO_3 , to 200° .



Iodic Acid, HIO_3 , is made by boiling iodine with concentrated nitric acid. It is a white crystalline solid.



Iodic acid forms salts called iodates. When iodine is dissolved in potassium hydroxide, potassium iodate is produced.



Uses of Iodine and its Compounds. A solution of iodine in alcohol, called tincture of iodine, is used for reducing swelling and inflammation. Potassium iodide is used in medicine in the treatment of goitre. Both potassium bromide and iodide are utilized in the manufacture of photographic films and plates.

Additional Experiments

EXPT.—To show the action of bromine on tin. Add a drop or two of bromine to a little finely granulated tin and warm gently. They unite with incandescence.

EXPT.—Oxidizing action of bromine. Add bromine water to sulphuretted hydrogen solution, and note the separation of sulphur.

EXPT.—Prepare iodine. Place a mixture of manganese dioxide and potassium iodide in a porcelain basin. Add sulphuric acid and warm. Cover the basin with an inverted filter funnel. The iodine condenses on the funnel.

EXPT.—By means of a pipette place a layer of chloroform or carbon disulphide at the bottom of a cylinder. Above it place carefully a layer of water and above that a layer of ether. Drop in a few crystals of iodine. Note the colours of the solutions.

EXPT.—Mix some dry aluminium powder with a little iodine and add a drop of water. The substances react immediately.

EXPT.—Grind up some damp iron filings with iodine in a mortar, to shew action of iodine on iron.

QUESTIONS

1. Compare the elements chlorine, bromine, and iodine in respect to their physical properties. Give reasons why they should be looked on chemically as belonging to the same family. How is hydrogen bromide prepared? Give a sketch of the apparatus used. Why cannot it be prepared in the same way as hydrogen chloride? (Scot. Univ. Entrance.)

2. Mention two natural sources of bromine, and indicate briefly how the element is obtained commercially. Describe a laboratory method for preparing bromine. Compare three physical properties of chlorine and bromine, and outline two sets of experiments you would perform to compare their chemical properties.

(London Matric.)

3. Describe how you would prepare and collect a small quantity of liquid bromine. Under what conditions does this element combine with hydrogen, and how does the compound so formed resemble and differ from the corresponding compounds of chlorine and iodine? (London Matric.)

4. Describe the appearance of the element iodine, and any experiments which you have performed, or seen performed, with it.
(Oxford and Camb. School Cert.)

5. From what natural sources is iodine obtained? Describe the methods for its extraction.

6. Describe and explain what you would observe on heating with concentrated sulphuric acid, (a) sodium chloride, (b) sodium bromide, (c) sodium iodide. What method would you adopt to prepare hydrobromic acid? Give full details.

(Scot. Leaving Cert.)

CHAPTER XXIX

SULPHUR. HYDROGEN SULPHIDE

SULPHUR is itself a useful substance, but its chief importance rests on the fact that it is the starting point in the manufacture of sulphuric acid, the most indispensable of all chemical substances to our great technical industries.

History. As the element is found in the free state in volcanic regions, it was known from very early times. It is mentioned in the Bible and in Homer (900 B.C.). The Greeks and Romans obtained it from Sicily, where it is found in large quantities, and used the fumes of burning sulphur (sulphur dioxide) for fumigating, and for bleaching cloth. Sulphur was regarded by the ancient chemists as 'the principle of fire,' and all metals were supposed to consist of sulphur and mercury in varying proportions. It was finally given a place among the elements by Lavoisier.

Occurrence and Production. Sulphur, also known as 'brimstone,' is found in the 'free' and 'combined' states, but the main world's supply comes from deposits of free sulphur in Sicily, Louisiana and Texas. In Sicily it is found mixed with lava and other rocks, which are quarried and burnt in a kiln. The sulphur melts and collects at the bottom and is run into moulds at intervals. Rock sulphur is impure and is refined by distillation in iron retorts. The first vapour condenses on the walls of the brick condensing chambers as the familiar yellow powder which we call 'flowers of sulphur.' As the temperature in the chambers rises, the condensed sulphur melts and is drawn off into wooden moulds, giving 'roll sulphur.'

In America the method of obtaining sulphur is entirely different. It is found in Louisiana and Texas in underground beds at a depth of 900 feet, from which it is mined by the 'Frasch process.' A bore is sunk to the sulphur bed and

four concentric pipes are driven down, the diameters of which are respectively 8, 6, 3, and 1 inches. Call these *A*, *B*, *C*, and *D*. Water superheated under pressure to 170° is sent down between *A* and *B* and between *B* and *C* to melt the sulphur. Compressed air is then pumped through the inner tube *D*, which forces a mixture of sulphur, water and air up between *C* and *D*. The mixture is run into large wooden vats, where the sulphur solidifies on cooling, and is so pure that it seldom needs refining. The output of the Louisiana and Texas deposits is over 2 million tons annually.

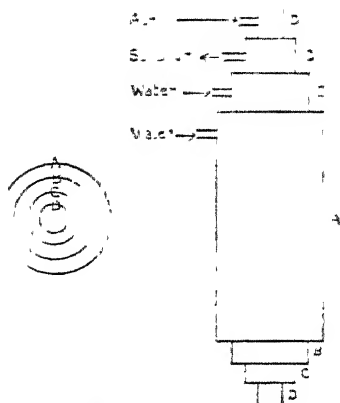


FIG 90 —The Frasch Process.

A certain amount of sulphur is recovered from by-products of manufacturing processes. The spent oxide from gas-works is, as we have seen, used in the manufacture of sulphuric acid.

In the Leblanc process for the manufacture of sodium carbonate, now almost obsolete, a waste product known as 'alkali waste' was for many years produced in large quantities. It contains calcium sulphide, CaS , and it has been found possible to recover the sulphur by a method which will be described later.

Combined Sulphur. Many metallic ores are found in nature as sulphides, and some of these are of great importance in the extraction of the metals. The chief source of copper is *copper pyrites*, $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$; of zinc, *zinc blende*, ZnS ; of lead, *galena*, PbS , of mercury, *cinnabar*, HgS . *Iron pyrites*, FeS_2 , is used to provide sulphur in making sulphuric acid. Sulphur is also found in combination in sulphates, such as *gypsum* or calcium sulphate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Allotropic Forms of Sulphur. Sulphur occurs in two distinct crystalline forms, **Rhombic** and **Monoclinic**. There are also several varieties of **Amorphous** sulphur.

Rhombic Sulphur is the stable form to which all the other forms return gradually after standing for some time. It is a pale yellow crystalline solid, soluble in carbon disulphide but

insoluble in water, and may be obtained by dissolving flowers of sulphur in carbon disulphide and allowing the solution to evaporate slowly.

EXPT.—Dissolve some powdered sulphur in carbon disulphide in a beaker. A small residue may be left of amorphous sulphur.

Filter into a basin and allow to evaporate slowly in the fume cupboard. Crystals of rhombic sulphur are left, which should be examined with a magnifying glass. Remember the caution already given regarding the use of carbon disulphide.

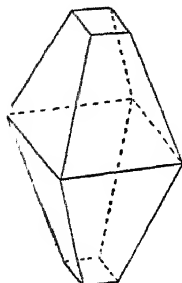


FIG. 91—Rhombic Sulphur

2. Monoclinic Sulphur. When rhombic sulphur is heated for some time above 96° , it changes slowly into monoclinic sulphur, forming crystals which are yellow and transparent and appear needle-like, but are in reality long prisms. At temperatures below 96° they gradually become opaque and crumble into minute crystals of rhombic sulphur. The easiest way of obtaining this variety is to melt sulphur in a basin or large crucible and allow to cool.

EXPT.—Melt a quantity of sulphur in a deep basin or large crucible. Allow to cool till a crust forms on the surface, the interior being still molten. Then pierce two holes in the crust with a glass rod (one to admit air) and pour out the liquid portion. Cut the crust round the edges and remove it. A mass of needle-

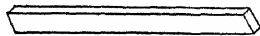


FIG. 92—Monoclinic Sulphur

shaped crystals of monoclinic sulphur is left. Examine these with a magnifying glass and lay the basin aside for a week. At the end of that time they will have crumbled into small rhombic crystals; they have returned to the stable form.

Rhombic sulphur changes into monoclinic on heating above 96° , and the monoclinic form is slowly transformed into the rhombic when kept below 96° . The temperature at which one crystalline form changes into another is called the **Transition Point**; in this case it is 96° . Both crystalline varieties of sulphur are soluble in carbon disulphide.

Amorphous Sulphur. When sulphur is heated, it melts at 114° to a pale yellow liquid. As the temperature is raised, the colour darkens and the liquid becomes thick and treacly. At 180° it is so viscous that it will not pour. After this it becomes more fluid again and finally boils at 444° . If it is poured into water when it becomes fluid for the second time, a substance is obtained which is elastic, almost like rubber, and is called **Plastic Sulphur**.

Expt.—Heat some sulphur in a small flask or tube kept for the purpose, as it is almost impossible to clean it afterwards. The tube should be gripped in a test tube holder. Observe carefully the various changes which take place, and when it has passed the viscous stage and is below the boiling-point pour it in a thin stream into cold water. Examine the stringy elastic substance formed. Shake some of it up in a test tube with carbon disulphide, pour the liquid into a basin and evaporate to test its solubility. Lay the plastic sulphur aside for a week and note that it gradually changes into rhombic sulphur, the stable modification below 96° . Test its solubility in carbon disulphide after standing.

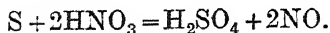
Plastic sulphur is an amorphous variety. It is insoluble, like the other amorphous forms, in carbon disulphide and returns to the stable form on standing.

Flowers of sulphur are mainly rhombic sulphur crystals, but also contain some amorphous sulphur insoluble in carbon disulphide.

Expt.—Warm a little flowers of sulphur very gently in a beaker, with excess of carbon disulphide. A white powder is left. Filter, and wash with more carbon disulphide. Examine it with a magnifying glass to see if it has a crystalline appearance.

Properties of Sulphur. Symbol, S. Atomic weight, 32. Sulphur boils at 444° , giving a red vapour, the density of which varies with the temperature. Sulphur forms compounds with many of the elements. With hydrogen it forms hydrogen sulphide, H_2S . When burned in oxygen it gives sulphur dioxide, SO_2 . When chlorine is passed over melted sulphur, sulphur chloride, S_2Cl_2 , is produced, a reddish yellow liquid. Sulphur unites directly with many metals, iron, copper, zinc and others, forming sulphides. Union takes place vigorously when the powdered metal is mixed with sulphur and heated, as we have already observed in the combination of iron and sulphur.

Strong nitric acid oxidizes sulphur on heating, giving sulphuric acid.



Uses of Sulphur. Crude or unrefined sulphur is used in the manufacture of sulphuric acid, in making sulphur dioxide and sulphites for bleaching wool and wood pulp, and in making carbon disulphide. Refined sulphur is used in making gunpowder, fireworks, matches and in medicine. Another important use is in the process of 'vulcanising' rubber, invented by Goodyear in 1839. Crude rubber does not retain its elasticity well. This is corrected and a better material obtained by heating the rubber with 10-12 parts of sulphur, when it is known as 'vulcanised' rubber. If 30 parts of sulphur are added, the well-known substance 'vulcanite' or 'ebonite' is produced.

Hydrogen Sulphide or Sulphuretted Hydrogen, H_2S .

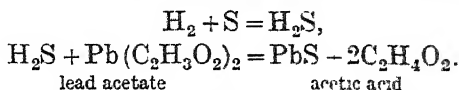
Occurrence. It is found in some mineral springs, the so-called 'sulphur waters,' and is also contained in the gases issuing from volcanoes. During the decay of animal and vegetable matter containing sulphur, hydrogen sulphide is given off. It is a product of the combustion of coal, and the blackening of silver exposed to air is due to traces of the gas in the atmosphere, combining with it to form black silver sulphide.

History. Hydrogen sulphide appears to have been known as far back as the time of Zosimus, about the beginning of the fifth century, and several references to the gas and its evil smell are found in the writings of the alchemists, who called it 'sulphurous vapour.' Scheele (1777) was the first to make a systematic investigation of the gas. He prepared it by the action of an acid on a sulphide, and also synthesised it by the direct union of hydrogen and sulphur. Scheele gave it the name 'inflammable sulphurous air.'

Preparation

1. Hydrogen sulphide can be prepared by synthesis of its elements. If sulphur is boiled in a wide test tube or boiling tube and a current of hydrogen gas passed through it, the issuing gas contains a small quantity of hydrogen sulphide. This may be tested by holding near the exit tube a piece of

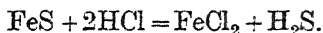
filter paper moistened with lead acetate. The paper becomes browned owing to the formation of lead sulphide.



The disagreeable smell of the gas may also be observed.

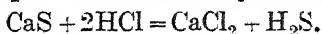
The quantity of hydrogen sulphide obtained in this way is small, as the gas is decomposed on heating.

2. The usual method of preparation is by the action of dilute hydrochloric or sulphuric acid on ferrous sulphide.



A Kipp's apparatus is used, as already described. Sticks of ferrous sulphide are placed in the centre bulb and dilute acid is poured in, with the tap open, until the sticks are just covered. A little time is allowed for the hydrogen sulphide to displace the air, the tap is closed and the apparatus is ready. As the ferrous sulphide generally contains iron, being made by heating iron with sulphur, the gas is usually mixed with hydrogen.

3. If gas free from hydrogen is required, it may be prepared from calcium sulphide and dilute hydrochloric acid.



Hydrogen sulphide is fairly soluble in water, so that it is best collected over hot water or by downward displacement.

EXPT.—Collect a few jars of hydrogen sulphide and carry out the following experiments, preferably in a fume chamber, owing to the poisonous nature of the gas.

1. Note the disagreeable odour, and test the gas with moist blue litmus paper.

2. Test with a lighted taper whether it is combustible or a supporter of combustion. Note the smell of sulphur dioxide when the gas burns.

3. Drop a piece of bright silver into a jar of the gas and leave it for a little time; it becomes blackened.

4. Burn a jet of hydrogen sulphide, and hold the flame against a porcelain basin containing water to keep it cool. A yellow film of sulphur is deposited.

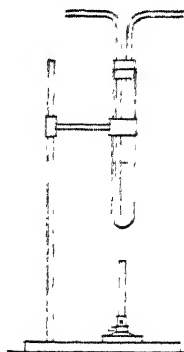


FIG. 93.

5. Find out whether it is an oxidizing or reducing agent. Expose a piece of moist starch iodide paper to the gas. Pass the gas through acidified potassium permanganate. What do the results of these tests indicate?

6. Invert a jar of chlorine over a jar of hydrogen sulphide and remove the plates. Observe the formation of sulphur.

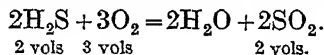
7. Place a little lead peroxide in a basin and direct a stream of the gas on to it.

8. Bubble a little of the gas through solutions of salts of mercury, lead, copper, cadmium, arsenic, antimony, and bismuth. Note the colours of the precipitates produced. Test the liquid before precipitation, and after the precipitate has settled, with blue litmus paper. In each case it has become acid.

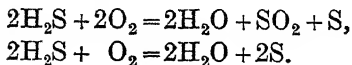
Properties of Hydrogen Sulphide. It is a colourless gas with an acid reaction, and has an unpleasant smell resembling rotten eggs. A silver egg-spoon in constant use soon becomes tarnished with a film of silver sulphide, as the white of egg contains sulphur, which is converted into hydrogen sulphide when the egg decays.

The gas is very poisonous—an atmosphere containing more than 1 part in 1000 is dangerous. The best antidote is to breathe a little dilute chlorine made by moistening bleaching powder with acetic acid, or to smell a chlorine water bottle.

Hydrogen sulphide is easily liquefied and is fairly soluble. Water dissolves $2\frac{1}{2}$ -3 times its own volume at ordinary temperatures. It burns in air or oxygen with a blue flame, giving sulphur dioxide and water, but does not support combustion.



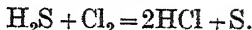
The proportion of 2 volumes to 3 makes the most explosive mixture. With an insufficient supply of air, the hydrogen has the first claim on the oxygen, and some sulphur may remain unburnt.



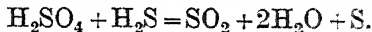
Hydrogen sulphide is decomposed by heat. When it is burned at a jet, the gas in the interior of the flame is dissociated into its elements, and if the flame be held against a cold porcelain basin, sulphur is deposited.

It is a reducing agent. As it is not a very stable compound, the hydrogen which it contains readily combines with oxygen.

Potassium permanganate solution is decolorised and potassium dichromate solution is turned green by the gas: they are both reduced. Chlorine takes away hydrogen to form hydrochloric acid, setting free sulphur.

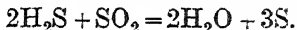


The gas cannot be dried by passing through sulphuric acid as they oxidize and reduce each other, sulphur being again set free.



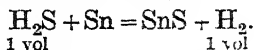
It is best dried by means of phosphorus pentoxide.

When hydrogen sulphide is mixed with sulphur dioxide in the presence of a little water, the sulphur dioxide is reduced.



This reaction is supposed to account for the deposits of sulphur found in volcanic regions, as both these gases are emitted by volcanoes.

Composition. Hydrogen sulphide is also commonly called sulphuretted hydrogen, and we should accustom ourselves to the use of both names, though the former gives the better indication of its chemical nature. As it can be made by the synthesis of hydrogen and sulphur, it is obvious that it can contain only these two elements. If a little metallic tin be heated in a tube containing hydrogen sulphide, with a manometer attached, as already described in the experiment illustrating the composition of carbon dioxide, it is found that the volume of gas in the tube remains unchanged.



Reasoning as in similar cases, we say,

- 1 volume of hydrogen sulphide gives 1 volume of hydrogen ;
- \therefore 1 molecule of hydrogen sulphide gives 1 molecule of hydrogen ;
- \therefore 1 molecule of hydrogen sulphide contains 1 molecule or 2 atoms of hydrogen, and its formula is H_2S_x .

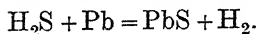
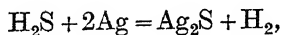
The relative density of hydrogen sulphide is 17, and its molecular weight is 34 ;

- \therefore 1 molecule contains $34 - 2 = 32$ parts of sulphur, and 32 is the weight of 1 atom of sulphur ;

\therefore the formula of hydrogen sulphide is H_2S .

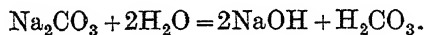
Sulphides. Sulphuretted hydrogen is an acid gas, and regarded as an acid is called hydrosulphuric acid. It forms salts known as sulphides. Note again the termination 'ide' applied to compounds formed from two elements, oxide, carbide, chloride, bromide, iodide, sulphide.

The gas acts on silver, lead and tin at ordinary temperatures, covering them with a coating of sulphide.

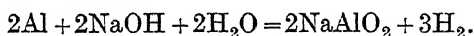


These, with some other metals, form sulphides when heated in sulphuretted hydrogen.

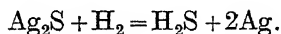
The following is a good method of cleaning tarnished silver. Put a piece of bright aluminium or zinc sheet, about 6×4 inches, in an earthenware or enamelled basin; a bare metal dish should not be used. Above this and in contact with it place the silver, then throw in two handfuls of washing soda and cover all with boiling water. The tarnish will soon disappear. Sodium carbonate is hydrolysed by water, giving sodium hydroxide,



The sodium hydroxide acts on the aluminium, giving sodium aluminate and hydrogen.



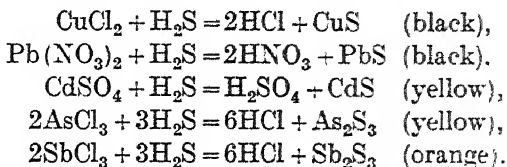
The hydrogen then acts on the silver sulphide, combining with the sulphur and removing it as hydrogen sulphide.



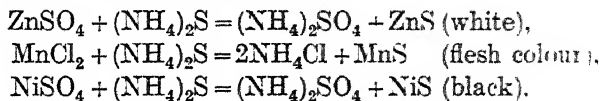
Sulphuretted hydrogen also blackens white lead paint, which is composed of lead carbonate, changing it to lead sulphide. As we have already learned, the colour is restored by hydrogen peroxide.

Most metals, with the chief exceptions of potassium, sodium and ammonium (the last is not a metal though it behaves chemically like one), form insoluble sulphides. These are precipitated when a stream of hydrogen sulphide is passed through a solution of a salt of the metal. Some of these sulphides have characteristic colours, by which the metal may be

identified, and the gas, or its solution in water, is used as a reagent in analysis.



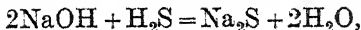
Observe that in each case an acid is formed in the reaction. Some of the sulphides are soluble in dilute acids, and are only precipitated from alkaline solutions, so that an alkaline sulphide is used for their precipitation.



Using ammonium sulphide as the reagent, salts of ammonium are obtained instead of salts of hydrogen, or acids.

EXPT.—Add a little ammonium sulphide to the following solutions: ferric chloride, FeCl_3 , nickel sulphate, NiSO_4 , cobalt nitrate, $\text{Co}(\text{NO}_3)_2$, zinc sulphate, ZnSO_4 , and manganese sulphate, MnSO_4 . Note the colours of the precipitates and write the equations.

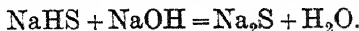
Hydrosulphuric acid is dibasic, as it contains two replaceable hydrogen atoms. Thus two sodium sulphides are possible. NaHS and Na_2S . When the gas is passed through sodium hydroxide solution, the normal sulphide is formed first,



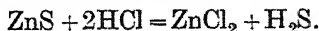
then the normal is converted into the acid sulphide or sodium hydrogen sulphide. Compare with the action of carbon dioxide.



To obtain a solution of the normal sulphide, take some sodium hydroxide solution and divide it into two equal parts. Saturate one part with hydrogen sulphide, then add the other part.



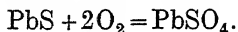
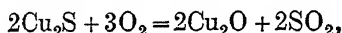
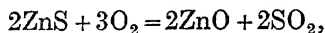
Most sulphides are decomposed by hydrochloric acid, giving a chloride and hydrogen sulphide.



Tests for Hydrogen Sulphide and Sulphides

1. A piece of filter paper moistened with lead acetate solution is blackened by the gas.
2. If the gas is passed through lead acetate solution a black precipitate is obtained.
3. Heat the substance with dilute or strong hydrochloric acid, and test the vapours with lead acetate paper.

Many metallic ores are found in nature as sulphides. Before the metal can be extracted from them it is usually necessary to transform them into oxides. This in most cases can be done by heating or 'roasting' them exposed to air, both the metal and the sulphur being oxidized. In some cases, sulphate as well as oxide is formed.



Additional Experiments

EXPT.—Heat some sulphur in a tube till full of vapour. Introduce hot copper spiral and observe combustion of copper.

EXPT.—Prepare hydrogen sulphide from antimony sulphide.

EXPT.—Arrange a train, (1) hydrogen generator, (2) and (3) wash bottles containing lead acetate solution, (4) glass bulb tube containing sulphur, (5) wash bottle with lead acetate. Heat the sulphur and pass stream of hydrogen. Bottle (2) absorbs any hydrogen sulphide, bottle (3) remains colourless, bottle (5) is blackened by lead sulphide.

EXPT.—Explode a mixture of 2 volumes of hydrogen sulphide with 3 volumes of oxygen.

EXPT.—Reducing action of hydrogen sulphide. Wet the inside of a litre flask with water and pass in a slow current of hydrogen sulphide and of sulphur dioxide. Note separation of sulphur.

EXPT.—Pass hydrogen sulphide through concentrated sulphuric acid to show reduction and precipitation of sulphur.

QUESTIONS

1. What are the natural sources of sulphur ? How is it obtained in a marketable form ? (London Matric.)

2. What do you understand by the term Allotropy ? Illustrate your answer by referring to the properties of two allotropic modifications of (a) sulphur, and (b) oxygen. Describe briefly the preparation of two allotropic forms of either of these elements. (Scot. Leaving Cert.)

3. A quantity of sulphur is gradually heated in a flask. Describe the changes you would expect to observe at successive temperatures from 120°C. to 440°C. How are crystals of rhombic and monoclinic sulphur obtained ? (Oxford and Camb. School Cert.)

4. From what sources is sulphur obtained ? Give an account of any *three* experiments you have performed, or seen performed, illustrating the properties of sulphur. How would you attempt to find whether the solid substances formed by passing (a) sulphur vapour, (b) hydrogen sulphide, over red-hot iron filings are the same ? (London Matric.)

5. How would you prepare some small crystals of ordinary rhombic sulphur ? How may ordinary sulphur be converted into plastic sulphur ? What is meant by saying that this modification is unstable at the ordinary temperature ? Describe the chief properties of plastic or amorphous sulphur, and state how its appearance and properties alter when it is kept. (London Matric.)

6. How would you obtain a specimen of hydrogen sulphide from sulphur ? How and under what conditions does hydrogen sulphide react with (a) oxygen, (b) sulphur dioxide, (c) copper chloride ? (Oxford and Camb. School Cert.)

7. Describe experiments by which the formula of the molecule of hydrogen sulphide can be determined. (Oxford and Camb. School Cert.)

8. Explain what is meant by the expression 'reducing agent.' Describe two experiments showing that hydrogen sulphide is a reducing agent. (London Matric.)

CHAPTER XXX

THE OXYGEN COMPOUNDS OF SULPHUR

Sulphur Dioxide. Sulphur may have a valency of 2, 4 or 6, and unites with oxygen in two proportions, giving sulphur dioxide, SO_2 , and sulphur trioxide, SO_3 .

Occurrence. Sulphur dioxide is emitted by volcanoes. It is also a product of the combustion of coal, and may consequently be found in the air of towns.

History. It was known to the Greeks and the Romans as a product of burning sulphur, and was used for fumigating and bleaching. Priestley (1774) prepared it by heating strong sulphuric acid with mercury, and Lavoisier (1777) determined its composition.

Preparation

1. We have already prepared sulphur dioxide by burning sulphur in oxygen.

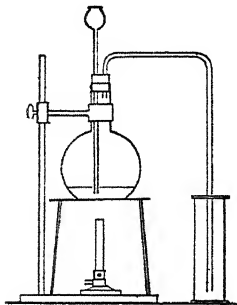


FIG. 94.

2. A common laboratory method is to heat concentrated sulphuric acid with copper turnings.

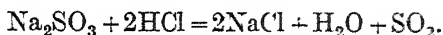


This is the main reaction, but cuprous sulphide, Cu_2S , is also a product and is left as a black residue after the action has ceased.

EXPT.—Place some copper turnings in a flask fitted with thistle funnel and delivery tube. Pour in sufficient strong sulphuric acid to cover the copper. Heat until the liquid begins to give off gas with effervescence. Then remove the burner, as the action will proceed without assistance. Collect

the gas by downward displacement. When the liquid in the flask has cooled, add an equal quantity of water, warm and filter. A black residue of cuprous sulphide, Cu_2S , is left on the filter. The filtrate contains copper sulphate, CuSO_4 , which may be obtained as blue crystals by evaporating partly and allowing to stand.

3. An easier method of preparation is by the action of dilute hydrochloric acid on sodium sulphite.



EXPT.—Fit up the apparatus as in the last experiment. Place in the flask a quantity of sodium sulphite crystals, and cover them with dilute hydrochloric acid. Warm. Collect the gas by downward displacement and fill two or three jars. Also prepare a solution by passing the gas for a few minutes through 100 c.c. of water in a beaker. Try the following experiments with the gas and its solution :

1. Test it with moist blue litmus paper.
2. Find out by means of a lighted taper whether it is combustible or a supporter of combustion.
3. Pass the gas into a wide test tube, surrounded by a freezing mixture of crushed ice and salt. Liquid sulphur dioxide collects in the tube. Pour it out, insert a thermometer into the liquid and note its boiling point.
4. Boil a little of the solution for a few minutes in a basin and add a drop of potassium permanganate solution; if all the sulphur dioxide has been boiled off the pink colour will remain unchanged.
5. Add a little of the solution to acidified solutions of potassium permanganate and potassium dichromate. Try its effect on starch iodide paper. Is it an oxidizing or reducing agent?
6. Heat some lead peroxide in a deflagrating spoon and lower it into a jar of the gas.
7. Test the bleaching action of sulphur dioxide gas and its solution on litmus, indigo, coloured flowers, etc.

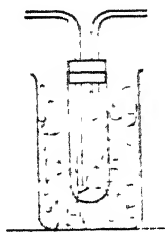
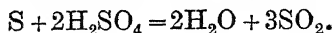
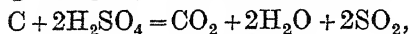
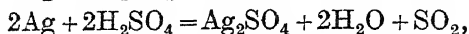
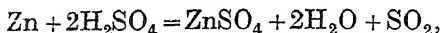


FIG 33

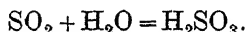
Make careful notes of all the reactions, and compare them with the explanations given under the heading of 'properties of sulphur dioxide.'

Concentrated sulphuric acid acts as an oxidizing agent in the second method given for the preparation of sulphur dioxide.

and it reacts with the following metals and non-metals in a similar way :



Properties of Sulphur Dioxide. It is a colourless gas with a choking smell, and is poisonous. It is not combustible, neither does it usually support combustion, but some metals which have a strong affinity for oxygen, such as potassium, sodium and magnesium, will continue to burn in the gas. Sulphur dioxide can be easily liquefied by a freezing mixture of salt and ice; its B.P. is -9° . Liquid sulphur dioxide can be bought in syphons which afford a convenient means of obtaining a supply of the gas. Water dissolves about 50 times its own volume of sulphur dioxide at ordinary temperatures. The solution has an acid reaction owing to the formation of sulphurous acid

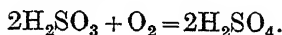


Sulphurous acid has not been obtained in the pure state, as it is unstable. When its solution is boiled, sulphur dioxide gas is driven off and water alone remains.

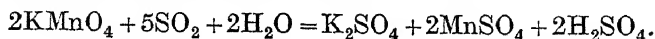
Sulphur dioxide is a reducing agent. Sulphur has a maximum valency of 6. Only 4 of the 6 bonds are employed in sulphur dioxide,

$\text{O}=\text{S}=\text{O}$, and the tendency is to take another atom of oxygen to form sulphur trioxide, $\text{O}=\text{S}=\text{O}=\text{O}$, which unites with water, giving sulphuric acid, H_2SO_4 , or $\text{O}=\text{S}(\text{O})_2\text{H}_2$

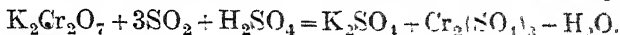
A solution of sulphur dioxide when exposed to air gradually becomes oxidized to sulphuric acid



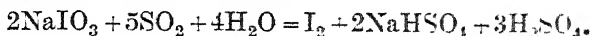
It is therefore a reducing agent. Potassium permanganate solution is reduced and decolorised.



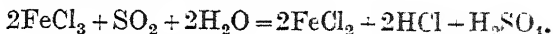
Acidified potassium dichromate is reduced and turns green.



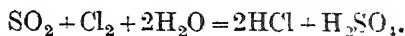
We have seen that sulphur dioxide is used to obtain iodine by the reduction of sodium iodate.



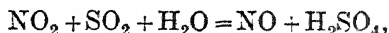
Ferric salts are reduced to ferrous salts.



Chlorine, bromine and iodine oxidize sulphur dioxide to sulphuric acid.



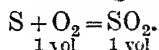
Nitrogen peroxide acts similarly,



and this reaction is used in the 'lead chamber' process for the manufacture of sulphuric acid

Bleaching Properties of Sulphur Dioxide. It bleaches many coloured substances. For example, rose petals and cloth dyed in 'magenta' lose their colours when moistened and introduced into a jar of the gas, but the colours are restored by dilute sulphuric acid. Chlorine bleaches by oxidation and sulphur dioxide by reduction. The colouring matter seems to be reduced but not completely destroyed, as oxidation in many cases restores it. Sulphur dioxide is a milder bleacher than chlorine, and is used in the treatment of materials which might be injured by the latter, such as straw, silk, wool, sponges and others. Fabrics bleached by sulphur dioxide unfortunately often revert to their original yellowish colour after frequent washing and exposure to oxidizing conditions.

Composition. When sulphur is burned in a measured volume of oxygen the volume of gas remains unchanged.



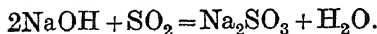
The volumetric composition may be demonstrated in the same manner as that of carbon dioxide, substituting sulphur for carbon, and using the same apparatus. The chain of reasoning by which its formula is established is also the same, and should be worked out by the student.

Uses of Sulphur Dioxide. Its use as a bleaching agent has already been described. It is also employed in the manu-

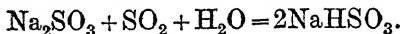
facture of sulphuric acid, in refrigerating plant (in the same way as ammonia), as an antichlor, and as a disinfectant.

Sulphites. Sulphur dioxide is the anhydride of sulphurous acid, H_2SO_3 . The salts of sulphurous acid are called sulphites. As the molecule of the acid contains two replaceable hydrogen atoms it acts as a dibasic acid, forming two salts, acid and normal.

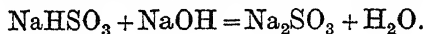
When sulphur dioxide is passed into sodium hydroxide solution, the normal sulphite is first formed.



Further action gives the acid sulphite or sodium bisulphite.

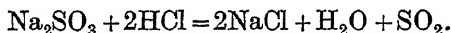


If some sodium hydroxide solution be divided into 2 equal parts, one part saturated with sulphur dioxide, and the other part mixed with it, normal sodium sulphite is obtained.



Calcium bisulphite, $\text{Ca}(\text{HSO}_3)_2$, is used in the manufacture of wood pulp.

When a sulphite is warmed with dilute hydrochloric acid sulphur dioxide is evolved.



Tests for Sulphur Dioxide and Sulphites

1. Sulphur dioxide and sulphurous acid may be recognised by the smell of burning sulphur.
2. A piece of filter paper dipped in potassium dichromate solution, acidified with sulphuric acid, is turned green by the gas and its solution.
3. Filter paper dipped in iodine solution is decolorised.
4. A sulphite warmed with dilute hydrochloric acid liberates sulphur dioxide, which may be identified by the above tests.

Sulphur Trioxide, SO_3 .

Preparation. It would seem a simple matter to oxidize sulphur dioxide to sulphur trioxide, as a solution of the dioxide, or sulphurous acid, gradually becomes oxidized to sulphuric

acid on exposure to air—that is, SO_2 becomes SO_3 , but gaseous sulphur dioxide does not unite readily with oxygen even when the gases are heated together.

We have already learned that many reactions are helped by employing a catalyst, and in this case the chemist again calls in the aid of one of these useful servants. Oxides of iron, copper and chromium are quite effective, but the most generally favoured is finely divided platinum, used in the form of 'platinised asbestos.' This is prepared by soaking asbestos fibre in a solution of platinum chloride, drying, and heating to 500° . The platinic chloride is decomposed by heat, chlorine is given off, and a finely divided residue of platinum is left upon the fibre.

Sulphur trioxide may be prepared in the laboratory in the following manner :

EXPT.—Oxygen from a cylinder and sulphur dioxide from a syphon of the liquid are passed through concentrated sulphuric acid, which serves the double purpose of drying the gases and showing their rate of flow. The gas mixture then passes through a combustion tube containing the catalyst, heated by a gas flame. Sulphur trioxide is formed as a white mist and passes into a flask which cool by a freezing mixture of ice and salt, where it condenses to an oily liquid, which gradually solidifies to a white crystalline solid. The temperature of the freezing mixture should not be below -9° , or sulphur dioxide will be liquefied.

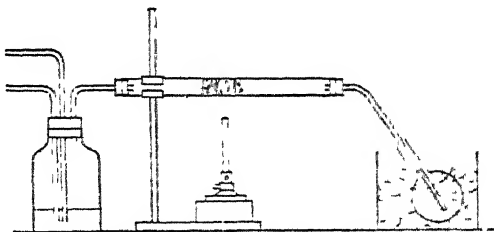
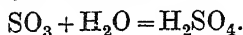


FIG. 96.

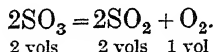
If a good specimen of sulphur trioxide, in the form of white silky needle-like crystals, is desired, it is best prepared by distilling 'oleum,' or 'fuming' sulphuric acid, which contains sulphur trioxide in solution, and condensing in a cooled receiver. The formula of oleum may be written, $\text{H}_2\text{S}_2\text{O}_7$ or $\text{H}_2\text{SO}_4 \cdot \text{SO}_3$.

Properties of Sulphur Trioxide. It may exist as a vapour, as a liquid, or as a white crystalline solid resembling fine

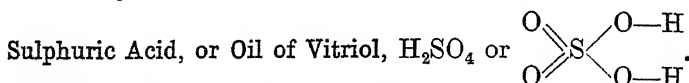
asbestos fibre. It reacts violently with water, giving out much heat, and forming sulphuric acid.



Sulphur trioxide is therefore the anhydride of sulphuric acid. It is soluble in concentrated sulphuric acid, forming oleum or fuming sulphuric acid, $\text{H}_2\text{S}_2\text{O}_7$. When the vapour is passed through a red-hot tube, it is decomposed into sulphur dioxide and oxygen.



Composition. Two volumes of sulphur trioxide give two volumes of sulphur dioxide and one volume of oxygen. From these proportions and the value of the vapour density, 40, the formula SO_3 can be calculated in the usual way.



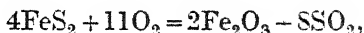
History. Ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, was known to the Romans as 'vitriol,' meaning 'a kind of glass.' By distillation of this substance the alchemists obtained an oily liquid, sulphuric acid, which Geber called 'oil of vitriol.' Basil Valentine, who lived in the earlier part of the fifteenth century, is said to have prepared the acid by burning sulphur with nitre in moist air, thus foreshadowing the modern chamber process. In 1675 Lemery described its preparation by burning sulphur and nitre under a glass bell in the presence of water, and the same method was first made use of on a commercial scale by Ward, at Richmond. Glass vessels were found unsuitable on account of their expense and fragility, so Roebuck (1746) substituted chambers built of lead in his works at Prestonpans, but otherwise the process remained the same. In the succeeding centuries many improvements were introduced into the 'chamber process,' the most modern being the use of oxides of nitrogen obtained by the oxidation of synthetic ammonia.

The Contact Process. The process of oxidation of sulphur dioxide to sulphur trioxide with the aid of a catalyst is known as the 'contact process,' and was discovered by Philips in 1831. Many attempts were made to make use of the process for the production of sulphuric acid on a large scale, but all ended in failure. It was found that after it had been a short time in use

the platinum catalyst became 'poisoned' and ceased to function. Also, the greater part of the white fumes of sulphur trioxide refused to dissolve in water and escaped into the air. After years of research, some German chemists discovered that the inactivity of the catalyst was due to poisoning by arsenic and dust in the sulphur dioxide and air. The sulphur dioxide had been obtained by burning iron pyrites, which usually contains some arsenic. When burned this was converted into arsenious oxide and passed with the gases over the catalyst. For some unknown reason, a small trace of arsenic quickly destroys the catalytic activity of platinum, and it is consequently necessary to purify the sulphur dioxide and air very thoroughly.

1. Preparation of Sulphuric Acid by the Contact Process

In the commercial process, which was established in 1901, the sulphur dioxide is obtained by burning sulphur or iron pyrites,



and air is used instead of oxygen, the best proportions being about 7 volumes of air to 1 volume of sulphur dioxide.

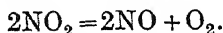
The mixture of gases from the pyrites burners passes into a 'dust' chamber, where it is cleaned by jets of steam, and is dried by passing through a tower packed with coke soaked in sulphuric acid. After cleaning, the gas must pass the Tyndall test—that is, a beam of light passing through it must show no dust particles. It then enters the contact chamber, which consists of a cylinder containing tubes packed with platinised asbestos, heated to 400° . The sulphur trioxide cannot be dissolved in water, but is absorbed in concentrated 97-98% sulphuric acid, giving the acid known as oleum. If 97-98% acid is required it is kept at that strength by continuous dilution with water.

The contact process has two great advantages over its competitor, the chamber process.

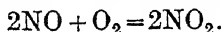
1. Owing to the careful purification of the materials, it gives a purer acid
2. Any lower strength of acid than oleum can be obtained simply by adding water.

2. Preparation of Sulphuric Acid by the Chamber Process

Sulphuric acid is also produced in this process by the oxidation of sulphur dioxide. The most effective oxidizing agent is nitrogen peroxide, NO_2 , which in the presence of water oxidizes sulphur dioxide to sulphuric acid and is itself reduced to nitric oxide



It then takes up oxygen to re-form nitrogen peroxide.



In this way nitric oxide acts as a catalyst, being alternately oxidized and reduced, so the process is continuous.

EXPT.—The process may be imitated on a small scale by taking a dry 6-litre flask, fitted with a rubber stopper containing 5 holes. The four substances which take part in the reaction are, sulphur dioxide, nitric oxide, oxygen, and steam. One tube is connected to a syphon of liquid sulphur dioxide, one to a gasholder containing nitric oxide and a third to a cylinder of oxygen. These

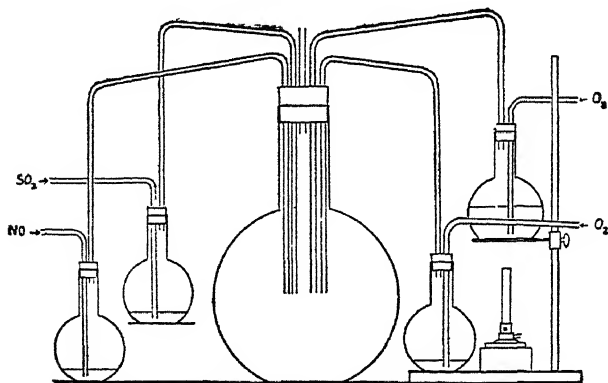


FIG. 97.—Manufacture of Sulphuric Acid.

three gases are dried by passing through sulphuric acid. The steam is supplied by bubbling oxygen through a flask containing water, which can be heated, the oxygen carrying the steam into the large flask. The fifth tube is an exit tube. Oxygen is first passed through to sweep out the air, then nitric oxide, and brown fumes of nitrogen peroxide immediately appear. Sulphur dioxide is then introduced at the same rate, and a little water vapour.

White crystals known as 'chamber crystals' form on the sides of the flask, and the colour of the gases becomes lighter. If more steam is blown in, the crystals dissolve, and in doing so set free oxides of nitrogen, forming sulphuric acid. If the stream of oxygen is now stopped, the nitrogen peroxide is gradually reduced to nitric oxide and the gases become almost colourless. On turning on oxygen once more the nitric oxide is oxidized to nitrogen peroxide.

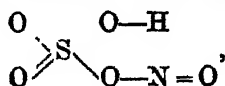
Test the liquid obtained with litmus paper. Dip a piece of filter paper in it and dry over the flame. Take a small quantity in a test tube and add a little barium chloride solution; a white precipitate indicates the presence of sulphuric acid.

Theory of the Process. The simplest explanation of the reactions which take place in the chamber process has already been given, that nitrogen peroxide in the presence of water oxidizes sulphur dioxide to sulphur trioxide, which then unites with the water to give sulphuric acid, according to the equation,

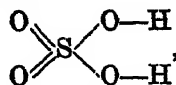


Another and more elaborate explanation is as follows:

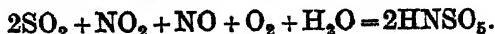
The experiment illustrates the formation of chamber crystals, when the proportion of water vapour is kept low. When it is increased the crystals decompose, setting free oxides of nitrogen. The chamber crystals form an intermediate product in the reaction and are composed of nitrososulphuric acid. This has the formula HNSO_3 , or graphically



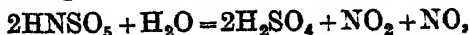
that is, sulphuric acid,



in which one hydrogen atom is replaced by the group NO, which when it acts as a radical is called the 'nitroso' group. The nitrososulphuric acid is first formed by the interaction of the gases, as in the equation,



It is then decomposed thus, giving sulphuric acid,



and is alternately reformed and decomposed throughout the process. Whether this takes place in the large-scale process when there is a sufficient supply of water, is doubtful.

The Commercial Process

1. The Pyrites Burners, or Sulphur Burners. The sulphur dioxide is generally obtained by burning iron pyrites, FeS_2 , in brick kilns.

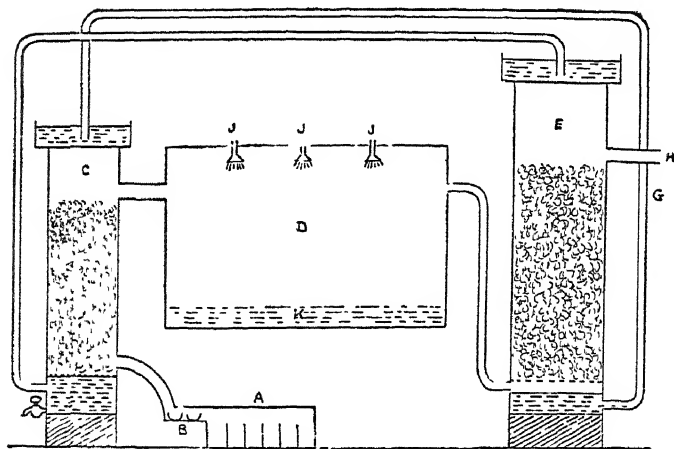
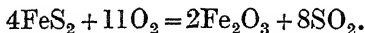
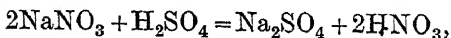


FIG 98 —Lead Chamber Process

- | | |
|---------------------|--|
| A Pyrites Burners. | F Pipe carrying 78% Acid to Gay Lussac Tower |
| B Nitre Pots | G Pipe carrying Nitrososulphuric Acid to Glover Tower. |
| C Glover Tower. | H Waste Gases to Chimney. |
| D. Lead Chamber. | J. Jets of Water or Steam |
| E. Gay Lussac Tower | K Chamber Acid. |

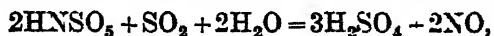
2. The Nitre Pots. The mixture of sulphur dioxide, with oxygen and nitrogen from the air, then passes over the nitre pots which contain sodium nitrate (Chile saltpetre) and concentrated sulphuric acid. The heat carried by the gases causes the following reaction,



and the nitric acid vapour breaks up into the oxides of nitrogen, NO and NO_2 .

In modern works the oxides of nitrogen are frequently obtained by the oxidation of ammonia by the Ostwald process.

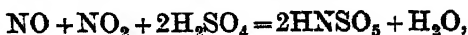
3. **The Glover Tower.** The hot gases then pass into the Glover tower. This is 20-30 feet high, and is packed with coke or flints. At the top of the tower are tanks from which two streams of sulphuric acid trickle down. One of these tanks is filled with strong acid containing oxides of nitrogen, pumped up from the Gay Lussac tower (to be described later). The other is filled with dilute acid from the lead chambers. There are then two descending streams, one of strong nitrated acid, the other of dilute acid. The entering gases meet the nitrated or nitrososulphuric acid and deprive it of oxides of nitrogen,



setting free sulphuric acid, and the expelled nitric oxide passes on with the other gases into the lead chambers. The stream of dilute acid is also concentrated by the heat of the gases, and the steam evolved also enters the chambers. About 25% of the output of acid from a plant comes from the Glover tower.

4. **The Lead Chambers.** There are usually three of these. They are built of sheet lead on which sulphuric acid, unless concentrated, has little action, and have a total capacity of about 150,000 cubic feet. The mixture of gases entering from the Glover tower contains sulphur dioxide, nitrogen peroxide, nitric oxide, oxygen, nitrogen and steam. More steam, or a fine spray of water, is blown into the lead chamber, and the reactions already described take place. Nitrososulphuric acid may be alternately formed and decomposed, and nitrogen peroxide is reduced to nitric oxide and re-oxidized. Sulphuric acid collects on the floors of the chambers, and is called 'chamber acid'; it is about 65-70% strength.

5. **The Gay Lussac Tower.** As the oxides of nitrogen merely undergo change, and are not lost, they pass with the remaining gases from the lead chambers into the Gay Lussac tower. The main object of this tower is to recover these oxides and make them available for further use. The Gay Lussac tower is 40-60 feet high, and is packed with coke over which a stream of strong sulphuric acid trickles. This acid absorbs the oxides of nitrogen, forming nitrososulphuric acid,



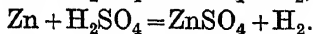
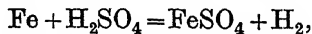
and is pumped from the bottom of the tower back to the tank at the top of the Glover tower, where, as we have seen, it is denitrated and the nitric oxide re-enters the lead chambers. Although theoretically there should be no loss of oxides of nitrogen, it is impossible in practice to avoid a little, so the supply is kept up from the nitre pots. The waste gas from the Gay Lussac tower, consisting mainly of nitrogen, passes up a chimney, which by its draught draws the gases through all the stages of the process.

The chamber acid, of 65-70% strength, is concentrated by heating in vessels of some acid-resisting material such as silica or ferro-silicon (an alloy of iron and silicon). Commercial concentrated sulphuric acid has a specific gravity of 1.84 and contains 98% of sulphuric acid. When a very pure acid is required, sulphur may be used instead of iron pyrites, and such acid is known as 'brimstone' acid.

Properties of Sulphuric Acid. It is a colourless, heavy, oily liquid, and is sometimes called vitriol. It boils at 338° , and an acid of 98.3% strength distills over unchanged. Owing to its high boiling-point it will displace acids of lower boiling-point from their salts. Thus it is used in the manufacture of nitric acid and hydrochloric acid.

Sulphuric acid has a strong affinity for water, and is consequently used for drying gases upon which it does not act chemically. When it is mixed with water great heat is given out, and as it has a very burning action on the skin, it is always advisable to pour acid into water when mixing, to avoid any splashing of concentrated acid. Sulphuric acid not only absorbs water, but it has the power of abstracting the elements of water from many substances. Examples have been given of its action on oxalic acid and paper.

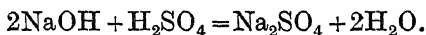
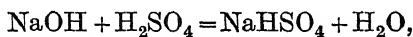
The oxidizing action of the concentrated acid on metals and non-metals has already been discussed. Dilute acid has no oxidizing action, but dissolves many of the metals, with evolution of hydrogen and formation of a sulphate.



Uses of Sulphuric Acid. It is perhaps the most indispensable of all chemicals used in industry, and there are very few articles in daily use which have not met sulphuric acid in one way or another during their manufacture. It is used in the

manufacture of nitric acid, hydrochloric acid, and sodium carbonate, in making the fertilisers ammonium sulphate and superphosphate, in making explosives, paints, dyes, glucose, alum, and in the textile, bleaching, and metallurgical industries.

Sulphates. Sulphuric acid is dibasic, as its molecule contains two atoms of replaceable hydrogen. It therefore forms acid and normal salts which are called sulphates. For example, there are two sodium sulphates—acid sodium sulphate or sodium bisulphate, NaHSO_4 , and normal sodium sulphate, Na_2SO_4 .



The sulphates are soluble in water, with the exception of those of calcium, strontium, barium, and lead. The soluble sulphates can be made by dissolving a metal, oxide, hydroxide or carbonate in dilute sulphuric acid and evaporating. The insoluble sulphates can be obtained by precipitation.

Sodium sulphate, Glauber's salt, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, and magnesium sulphate, Epsom salt, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, are used medicinally. Three crystalline sulphates are known as the 'vitriols,' green vitriol or ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, white vitriol or zinc sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and blue vitriol or copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Alums. There is an important series of double sulphates known as the 'alums.' Common alum or potash alum is made by mixing hot solutions of potassium sulphate and aluminium sulphate. On cooling, octahedral crystals of a double sulphate of potassium and aluminium separate out. The formula of the salt is $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. Potash alum is a typical member of its class, each of which consists of the sulphate of a monovalent metal united with the sulphate of a trivalent metal according to the general formula, $\text{M}_2'\text{SO}_4 \cdot \text{M}_2''(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. M' may be potassium, sodium or ammonium, and M'' may be iron, chromium, aluminium, manganese or cobalt. By using different combinations of these metals a large number of alums can be prepared. The alums are isomorphous with each other—that is, they crystallise in the same form, and a crystal of one of them suspended in a solution of any other will continue to grow. In this way it is possible to make a crystal consisting of different coloured layers.

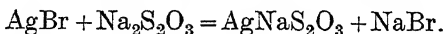
Test for Sulphuric Acid and Sulphates

To the solution add dilute hydrochloric acid and a few drops of barium chloride solution. A white precipitate of barium sulphate shows the presence of sulphuric acid or a sulphate.

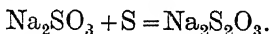
Thiosulphuric Acid, $\text{H}_2\text{S}_2\text{O}_3$. This acid is chiefly important on account of one of its salts, sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, which is used by photographers under the name of 'hypo,' a contraction of the old name of the salt 'hyposulphite of soda.'

Photography. A photographic plate or film is coated with an emulsion consisting of finely divided silver bromide and gelatine. On exposure to light in a camera the silver bromide undergoes a change, proportionate to the intensity of the light falling upon it, which may be chemical but is now generally considered to be physical. The plate is then immersed in a 'developing solution,' and the altered bromide only is reduced to metallic silver, giving a black deposit varying in thickness. If the plate were then exposed to light, the unchanged silver bromide would also be acted upon and the negative would be spoilt. The image must be 'fixed' by treatment with a solution of hypo, which dissolves off the unchanged bromide and leaves the black deposit of silver unaffected. The plate at this stage is called a 'negative,' as light and shade are reversed; the blackest parts of the plate correspond with the brightest parts of the object photographed, and *vice versa*. In order to reverse this again and obtain a positive, a piece of printing paper, which may be prepared with silver bromide as in 'gaslight' paper or silver chloride as in 'printing out' paper, is placed in contact with the negative and exposed to light. The paper which underlies the blacker and denser parts of the silver deposit is less affected by the light than that under the clearer and thinner parts, so that light and dark on the negative becomes respectively dark and light on the paper, and the light and shade of the subject is correctly rendered.

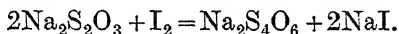
The equation for the fixing action of sodium thiosulphate is



Sodium thiosulphate is made by boiling sodium sulphite with sulphur.

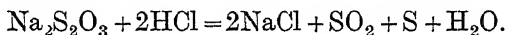


It is used in volumetric analysis as a reagent for the estimation of iodine in solution.



The products are sodium tetrathionate and sodium iodide.

Test for a Thiosulphate. When a solution is boiled with dilute hydrochloric acid, sulphur dioxide is evolved and sulphur is precipitated. Compare with sulphite.



Additional Experiments

EXPT.—Bleach violets or roses with sulphur dioxide, and restore the colour with chlorine water.

EXPT.—Pass sulphur dioxide into hot ferric chloride solution. Note reducing and decolorising effect.

EXPT.—Invert a jar of sulphur dioxide over strong caustic soda solution. Observe absorption.

EXPT.—Normal and acid sulphites. Make 100 c.c. of strong caustic soda solution. Take 50 c.c. and pass sulphur dioxide through it till saturated. Divide this solution into 2 equal parts. Evaporate one to crystallisation. To the other add 25 c.c. of the caustic soda solution and crystallise. Compare the appearance and reactions of the two sulphites.

EXPT.—Melt some potassium nitrate in a porcelain basin, and throw in one or two pieces of roll sulphur.

EXPT.—Place some cane sugar in a cylinder. Damp the sugar slightly with water and add a little concentrated sulphuric acid. Note swelling and charring.

EXPT.—Prepare normal and acid sodium sulphates.

EXPT.—Test the action of sulphuric acid, strong and dilute, on metals.

EXPT.—Find the basicity of sulphuric acid. Prepare 200 c.c. of dilute sulphuric acid, 1 part of acid to 3 parts of water. Neutralise 50 c.c. with caustic soda and crystallise. Again take 25 c.c., neutralise with caustic soda and add 25 c.c. of the acid, evaporate and crystallise. Take a third portion, of 20 c.c., neutralise, add 40 c.c. of the acid and crystallise. Only 2 kinds of crystals are formed.

QUESTIONS

1. Give a detailed account of the method you would employ to prepare sulphur dioxide in the laboratory. Write a note on the reactions involved. State the properties of the gas, and contrast the bleaching action of sulphur dioxide with that of chlorine.

(Scot. Leaving Cert.)

2. How would you prove experimentally that the weight of the product obtained when sulphur is burned in oxygen is greater than that of the sulphur which has disappeared? Draw a diagram of the apparatus you would use. How may the gaseous product be regained after this experiment?

(London Matric.)

3. An excess of chlorine water was added to 50 c.c. of a solution of sulphur dioxide. An excess of barium chloride (BaCl_2) solution was then added and the resulting precipitate, after filtering, washing, and drying weighed 0.5202 gram. Calculate the volume of sulphur dioxide at N.T.P. which was dissolved to make the original solution. ($\text{Ba} = 137$; $\text{S} = 32$.)

(London Matric.)

4. How would you obtain the following derivatives from sulphuric acid?—liquid sulphur dioxide, acid sodium sulphate, sodium thiosulphate. Describe the properties of sulphites.

(Oxford and Camb. School Cert.)

5. Give a short account of the 'contact' process for the manufacture of sulphuric acid. What advantages does it have over the 'chamber' process?

6. Give a sketch of the various stages in the manufacture of sulphuric acid by the 'chamber' process, and discuss the chemical reactions which are involved.

7. Describe the reaction which takes place when copper is heated with concentrated sulphuric acid. The resulting gas is passed into (a) litmus solution, (b) chlorine water, and (c) a solution of hydrogen sulphide. What would be observed in each case, and what explanations would you give of the results obtained?

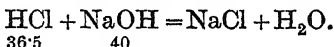
(London Matric.)

8. What is the chemical composition and the more correct name of 'hypo,' used in photography? For what purpose is it used?

CHAPTER XXXI

STANDARD SOLUTIONS. VOLUMETRIC ANALYSIS

WHEN an acid solution is carefully added to an alkaline solution coloured with litmus, a visible neutral point, generally called the 'end point,' is reached, when they have exactly neutralised each other and the solution is neither acid nor alkaline to litmus. The acid and alkali have combined to form a salt and water.



From the equation we see that 36.5 grams of hydrochloric acid neutralise 40 grams of sodium hydroxide. If then we take 36.5 grams of hydrochloric acid and dilute it with water to a volume of 1 litre, and take 40 grams of sodium hydroxide, dissolve in water, and dilute to 1 litre, these volumes will exactly neutralise one another when mixed. Also any given volume of one solution will exactly neutralise an equal volume of the other. The solutions are in fact equivalent.

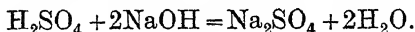
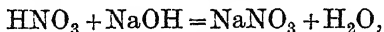
To a solution prepared of a definite known strength, the term 'standard solution' is applied. Standard solutions are used in chemical analysis for measuring the quantities of acids, alkalies, and many other substances, contained in solutions of unknown strength. This process is known as Volumetric Analysis.

Volumetric Analysis. A definite strength of standard solution is usually employed called a Normal Solution. One litre of a normal solution of acid or alkali contains 1 gram equivalent of the substance.

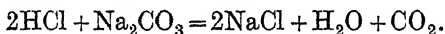
One gram equivalent of an acid is that weight in grams which contains 1 gram of replaceable hydrogen. The formula of hydrochloric acid is HCl , and the molecular weight in grams is $1 + 35.5 = 36.5$, which contains 1 gram of hydrogen, therefore 36.5 grams is the weight of 1 equivalent of hydrochloric acid. Nitric acid, HNO_3 , has a molecular weight of $1 + 14 + 48 = 63$,

which contains 1 gram of hydrogen, therefore 63 grams is the weight of 1 equivalent of nitric acid. Sulphuric acid, H_2SO_4 , has 2 replaceable hydrogen atoms in its molecule, therefore the molecular weight, $2 + 32 + 64 = 98$ grams, contains 2 grams of hydrogen, and the equivalent weight is $\frac{98}{2} = 49$ grams. It follows that the equivalent of a monobasic acid is equal to its molecular weight, that of a dibasic acid is half, and that of a tribasic acid is one-third of its molecular weight.

One gram equivalent of an alkali is that weight which will exactly neutralise 1 gram equivalent of an acid.



The molecular weight of sodium hydroxide is $23 + 16 + 1 = 40$, and this weight neutralises 1 gram equivalent of acid; accordingly 1 gram equivalent of sodium hydroxide is 40 grams. What about sodium carbonate, Na_2CO_3 ? The molecular weight is $46 + 12 + 48 = 106$. This neutralises 2 equivalents of hydrochloric acid.



The equivalent of sodium carbonate must then be $\frac{106}{2} = 53$ grams. From these considerations it follows that a given volume of a normal solution of any acid will neutralise exactly the same volume of a normal solution of any alkali. Standard solutions weaker or stronger than normal are often used, particularly a Decinormal solution, which contains $\frac{1}{10}$ of a gram equivalent per litre. A normal solution is usually indicated by the letter N, thus N. H_2SO_4 means normal sulphuric acid, twice normal is 2N, decinormal is $\frac{\text{N}}{10}$ and so on.

To make a normal solution of hydrochloric acid. As the strength of commercial concentrated acid varies, it is difficult to measure or weigh it with sufficient exactness. The best method is to measure out roughly the volume which contains 36.5 grams or 1 equivalent, dilute this to 1 litre with water and standardise it—that is, measure its exact strength by means of a standard alkaline solution. Of course it is not absolutely necessary to make up 1 litre of normal solution each time, any multiple or fraction of a litre can be made, taking the same multiple or fraction of the gram equivalent.

Let us suppose the specific gravity of the concentrated acid is 1.15; it is then about 30% strength. If it were 100% strong, 36.5
 $\frac{36.5}{1.15} = 32$ c.c. would be sufficient to obtain 36.5 grams of acid. As it is only 30%, $\frac{32 \times 100}{30} = 107$ c.c., are required. This

method of calculation can also be applied to nitric and sulphuric acids, the gravities can be ascertained by means of a hydrometer, and the percentage strength found from tables.

Measure 110 c.c. of concentrated hydrochloric acid in a graduated cylinder, and pour it into a litre flask. Add water gradually, shaking to assist mixture, and finally fill up to the mark on the neck of the flask. Cork tightly and invert the flask a few times to make sure that mixture is complete. Wash out a bottle of suitable size with a few c.c. of the acid, transfer the solution to it and affix a label. As the solution is only approximately normal, it must be standardised. This is best done by means of pure anhydrous sodium carbonate.

To make a normal solution of sodium carbonate. As this salt can be obtained in a very pure state, we need only weigh out 1 equivalent or 53 grams, dissolve in water and dilute to 1 litre. Weigh a clock glass or a small beaker to one decimal place, then add to the weights 53 grams. With a knife blade place sodium carbonate on the glass until the pointer of the balance swings an equal number of divisions on each side of the centre point. Place a filter funnel in the mouth of a litre flask, wash the sodium carbonate into the flask with a jet of warm water, and wash the funnel. Add more water and shake until it is all dissolved, then fill up to the mark and invert the corked flask half a dozen times to ensure complete mixing. Transfer the solution to a labelled bottle, as already described.

Note.—The preparation of these solutions may be done by teacher or pupil, as is most convenient.

Expt.—Wash out a burette with a few c.c. of the prepared hydrochloric acid, allow to drain and fix it in a stand. Fill the burette with the acid to above the zero graduation, using a small dry filter funnel. Remove the funnel and observe that the upper surface of the liquid is concave. This concave surface is called the *Meniscus*, and the bottom of the curve is usually taken in reading the level of the liquid. A piece of white paper with two slits cut in it and slipped over the burette gives a light background and makes reading easier. In taking a reading the eye should be at

the same level as the meniscus. Run the acid out of the burette, drop by drop, till the bottom of the meniscus touches the zero graduation mark. All is now ready for the standardisation, or, as it is usually called, the **Titration**. Take a 20 c.c. pipette, suck up into it 2-3 c.c. of the sodium carbonate solution, run this round the bulb to wash it out, and empty it again. Then fill up to the mark with the solution, and run it into a small flask standing on a sheet of white paper, blowing out the last drop. In order to show the neutralisation point or **End Point**, we require to add an **Indicator**, so called because it indicates acidity or alkalinity by a change of colour. Litmus is an indicator; there are also methyl orange, phenolphthalein and others. In this case add 1 or 2 drops of methyl orange, just sufficient to give the liquid a light yellow colour; too much of the indicator gives a doubtful end-point. Place the flask under the burette and run in the sulphuric acid slowly, so as not to overshoot the mark, swirling the liquid round occasionally to keep it mixed. A little practice enables one to see by the lingering of the pink colour when the end-point is near, which, with methyl orange, is the final change of the liquid from yellow to pink. Now read the graduation at the bottom of the meniscus; this shows how many c.c. have been used. Make three or four titrations and tabulate your results.

	Hydrochloric Acid	Sodium Carbonate
1.	19.0 c.c.	20 c.c.
2.	19.4 c.c.	20 c.c.
3.	19.5 c.c.	20 c.c.
4.	<u>19.5 c.c.</u>	<u>20 c.c.</u>
Mean	- 19.45 c.c.	20 c.c.

There should not be a difference of more than $\frac{1}{10}$ of a c.c. between successive titrations; an obviously incorrect result, like 1. above, should be neglected.

We find then that 19.45 c.c. of hydrochloric acid neutralises 20 c.c. of normal sodium carbonate. The acid must be slightly stronger than normal, as a less volume of it is required. Now it would be possible, by adding a calculated amount of water to the acid, to make it exactly normal strength, but this is a difficult and tedious operation. A quicker and more accurate way is to calculate the 'normality' of the solution. Divide 20 c.c.

by 19.45; $\frac{20}{19.45} = 1.03$, this is the normality—that is, the solution contains 1.03 times as much hydrochloric acid as an equal volume of a normal solution. The figure 1.03 is commonly called the 'normality factor,' and should be marked on the label of the bottle thus, 1.03N. HCl.

As the solution is stronger than normal, if water were added to convert it into a normal solution, its volume would be increased. Consequently, if the acid is used as a standard solution in other titrations, the number of c.c. used must be multiplied by 1.03 to obtain the equivalent number of c.c. of normal solution. It is unnecessary to have any standard solutions of exactly normal or decinormal strength, as long as we know the normality factor. If the solution is weaker than normal, the factor will of course be less than unity.

The weight of dissolved substance in a litre of solution is sometimes required. In that case, multiply the number of grams in a litre of normal solution, or the gram equivalent by the normality factor. In the above example,

$$36.5 \times 1.03 = 37.6;$$

the solution contains 37.6 grams of hydrochloric acid per litre.

If sodium carbonate is merely required for the purpose of standardising an acid quickly, the following method is simpler and more economical. Weigh out about 1 gram of pure sodium carbonate, wash into a flask, add indicator and titrate with the acid to be standardised exactly as in the previous experiment. Suppose 1.15 grams have been weighed

By theory, 53 grams of $\text{NaCO} = 1$ litre of normal solution.

$$\begin{array}{rcllcl} \text{and } \frac{53}{1000} = 0.053 & & & & & \\ \text{and } 1.15 \text{ grams} & = & \frac{1.15}{0.053} & & & \end{array} \quad \begin{array}{l} \text{,,} \quad \text{,,} \quad = 1 \text{ c.c.} \quad \text{,,} \quad \text{,,} \\ \text{,,} \quad \text{,,} \quad = 21.7 \text{ c.c.} \quad \text{,,} \quad \text{,,} \end{array}$$

Let X be the number of c.c. of acid required for titration, then the normality factor is $\frac{21.7}{X}$.

Two or three portions should be weighed and the factor calculated in each case. The factors ought to agree to two places of decimals, any obviously bad result being rejected.

To prepare a litre of normal sodium hydroxide. One equivalent is 40 grams, but the substance cannot be weighed accurately as it quickly absorbs moisture and carbon dioxide from the air, so the solution must be standardised. Weigh roughly 42 grams of pure stick caustic soda on a clock glass. Transfer to a litre flask, dissolve in water, and after the solution has cooled dilute up to the mark and mix thoroughly. Draw out 20 c.c. in a pipette, run it into a flask and titrate with standard hydrochloric acid. Phenolphthalein indicator may

be used. It gives a red colour with alkali and is colourless with acid. The end point in this titration is the disappearance of the pink colour. All other details are exactly the same as in the titration of sodium carbonate.

EXPT.—The choice of an indicator. Carry out several titrations of normal sodium carbonate with normal hydrochloric acid. Use first methyl orange, next litmus, and finally phenolphthalein. Observe that the end-point appears earlier with the last two than with methyl orange. When the carbonate is decomposed by the acid, carbon dioxide is formed and dissolves in the water, giving carbonic acid to which litmus and phenolphthalein are sensitive. Boil the solution containing the litmus; carbon dioxide is given off and the blue colour returns. Methyl orange should be used in any titration involving a carbonate. Phenolphthalein is not very sensitive to ammonia, and cannot be used in titrating this alkali. Measure 6 c.c. of strong ammonia in a graduated cylinder, dilute with water to 100 c.c. and titrate portions of this with standard acid, using first methyl orange, then phenolphthalein as indicators. Observe difference in end-point.

EXPT.—To find the percentage of sodium carbonate in crystalline sodium carbonate or washing soda, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. Weigh about 10 grams of the crystals in a beaker or clock glass. Dissolve in water, transfer to a 250 c.c. flask and dilute to the mark. Mix thoroughly. Take 50 c.c. and titrate with normal hydrochloric acid, using the proper indicator. Set down your results in this way.

Weight of beaker	-	-	-	50	grams
Weight of beaker + soda	-	-	-	60.1	grams
Weight of soda	-	-	-	10.1	grams
Titration.	HCl corrected to normal			Soda.	
1	14.1 c.c.			50 c.c.	
2	14.0 c.c.			50 c.c.	
3	14.1 c.c.			50 c.c.	

14.1 c.c. of N. HCl neutralises 50 c.c. of the soda solution ;

$$\therefore \text{the normality is } \frac{14.1}{50} = 0.282 ;$$

$$\therefore 1 \text{ litre contains } 53 \times 0.282 = 14.94 \text{ grams ;}$$

$$\text{and } 250 \text{ c.c. contains } \frac{14.94}{4} = 3.73 \text{ grams ;}$$

\therefore 10.1 grams of soda contain 3.73 grams of Na_2CO_3 , and this is equivalent to 37%. What is the theoretical value ?

To make a normal solution of sulphuric acid. Concentrated sulphuric acid usually has a specific gravity of 1.84 and may be 95%–98% strength. To make a litre of normal acid 49 grams of H_2SO_4 are required. To find the volume in c.c. of 49 grams of 1.84 acid, divide 49 by 1.84; $\frac{49}{1.84} = 26.6$ c.c. It is

best, however, to be on the safe side and take 29.30 c.c. Measure the acid in a graduated cylinder and pour it into a litre flask half full of water. When the liquid has cooled, fill up to the mark with water and mix thoroughly. Standardise with $\text{N} \cdot \text{Na}_2\text{CO}_3$ or $\text{N} \cdot \text{NaOH}$ in the manner already described and find the normality factor.

EXPT.—To find the strength of the bench dilute hydrochloric acid, using normal sodium hydroxide.

EXPT.—To find the equivalent of magnesium. Weigh out about 0.2 gram of clean magnesium ribbon. Wash out a burette with normal sulphuric acid, and fill it up to the zero graduation. Run 50 c.c. into a flask and add the magnesium. When dissolved, titrate the excess of acid with normal sodium hydroxide.

1 litre or 1 equivalent of normal sulphuric acid dissolves 1 equivalent of magnesium.

Let x = number of c.c. of normal alkali used,
then $50 - x$ = number of c.c. of acid used in dissolving magnesium.

Calculate the weight of magnesium which would be dissolved by 1 litre of acid; this is the equivalent weight.

$$\frac{1000}{50 - x} \times \text{weight of magnesium used} = \text{equivalent}.$$

EXPT.—The equivalents of zinc and aluminium can be found by a similar method, using hydrochloric acid.

Use of Potassium Permanganate in volumetric analysis. Potassium permanganate, KMnO_4 , on account of its oxidizing properties, is used in the estimation of many oxidizable substances. We have seen in Chap. XXV that 2 molecules of permanganate give 5 atoms of oxygen which are available for oxidizing purposes.



That is, 316 grams of KMnO_4 give 80 grams of oxygen.

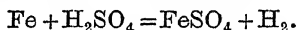
The equivalent of oxygen is 8, therefore 80 grams = 10 equivalents ;

\therefore 1 equivalent of potassium permanganate = $\frac{316}{10}$ = 31.6 grams.

But as it is invariably used as a decinormal solution, $\frac{N}{10}$, 1 litre of decinormal or $\frac{N}{10}$ KMnO_4 contains 3.16 grams.

EXPT.—To make a solution of potassium permanganate. Weigh 3.16 grams of the salt. Transfer to a large beaker and dissolve in water. It dissolves slowly, so pour off the solution into a litre flask, add more water in the beaker, and repeat the process till it is all dissolved. Fill the flask with water up to the mark and mix thoroughly.

EXPT.—To standardise the permanganate solution. This may be done by ferrous sulphate solution prepared from pure iron wire. Take a 300 c.c. flask, fit it up with a one-hole cork, carrying a leading tube bent at right angles and dipping into a beaker of water. Weigh out about 1 gram of iron wire in small pieces. Fill the flask half full with dilute sulphuric acid and drop into it a crystal of sodium carbonate, which will cause evolution of carbon dioxide to displace the air in the flask. This is intended to prevent oxidation of the ferrous sulphate. Add the iron wire, cork tightly and warm till the iron is completely dissolved and no more hydrogen passes through the water in the beaker.



Have some water ready which has been boiled to expel all dissolved oxygen, and afterwards cooled under the tap. Then cool the ferrous sulphate quickly under the tap, transfer to a 250 c.c. flask, washing out the original flask carefully, and dilute to the mark with the boiled water (alternatively the whole operation may be carried out in one flask). Mix thoroughly. Take 50 c.c. in a small flask for a titration. Potassium permanganate acts as its own indicator. When added to ferrous sulphate it is decolorised, and only when all the ferrous sulphate has been oxidized to ferric sulphate does the pink tint persist. To carry out a titration, run the permanganate solution from a burette into the ferrous sulphate with shaking, till a faint permanent pink tint appears; this is the end-point.

	Permanganate.	Ferrous Sulphate.
1	36.6 c.c.	50 c.c.
2	36.5 c.c.	50 c.c.
3	36.6 c.c.	50 c.c.

Let the weight of iron dissolved be 1 gram.

Then the weight of iron in 50 c.c. of ferrous sulphate is 0.2 gram ;

∴ 36.6 c.c. of permanganate oxidizes 0.2 gram of iron ;

∴ 1 c.c. " " $\frac{0.2}{36.6} = 0.0054$ gram of iron.

Theoretically, 1 c.c. of $\frac{N}{10}$ permanganate oxidizes 0.0056 gram of iron ;

∴ the normality factor is $\frac{0.0054}{0.0056} = 0.97$.

EXPT.—The standard permanganate may then be used to estimate the percentage of iron in crystalline ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, or in ferrous ammonium sulphate, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. The latter salt can be obtained very pure, is not readily oxidized by air, and is frequently used for standardising permanganate solution. Weigh about 7 grams of ferrous sulphate or 10 grams of ferrous ammonium sulphate. Dissolve in cold boiled water in a 250 c.c. flask, add some dilute sulphuric acid, and make up to the mark. Take 20 c.c. for titration with $\frac{N}{10}$ permanganate. Calculate the percentage of iron.

EXPT.—To estimate the percentage of iron in ferric alum, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. The iron is first reduced to the ferrous state. Weigh about 5 grams, transfer to a 300 c.c. flask. Add about 100 c.c. of water and 100 c.c. of dilute sulphuric acid and dissolve the salt. Fit the flask with a Bunsen valve. This consists of a piece of rubber tube with a slit $\frac{1}{2}$ inch long cut in it. It is slipped over a piece of glass tube, passing through the cork of the flask, and its upper end is stopped by a piece of glass rod. The slit permits the escape of steam from the flask, but does not admit air. Drop into the flask some pieces of granulated zinc and warm till the zinc has dissolved. Cool under the tap, transfer the contents to a 250 c.c. flask, and make up to the mark with boiled water. Mix and titrate 50 c.c. portions with potassium permanganate. Calculate as before.

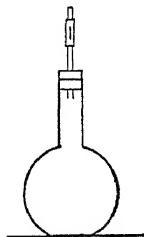
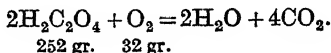


FIG. 99.

EXPT.—To estimate the percentage of oxalic acid in the crystalline substance. Weigh about 1 gram of oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. Transfer to a 250 c.c. graduated flask, dissolve in water and dilute to the mark. Mix thoroughly. Take 50 c.c. in a small flask for titration, add 50 c.c. dilute sulphuric acid and heat to about 60° , as the action is very slow in cold solution. Then titrate with $\frac{N}{10}$

permanganate, until a faint permanent pink colour is obtained.



Two gram molecules of oxalic acid or 252 grams are oxidized by one gram molecule or 32 grams of oxygen,

\therefore 63 grams of oxalic acid are oxidized by 8 grams of oxygen, but 8 grams of oxygen = 1 equivalent,

\therefore 63 grams of oxalic acid = 1 equivalent,

and 1 litre of $\frac{\text{N}}{10}$ oxalic acid will contain 6.3 grams.

\therefore 1 litre of $\frac{\text{N}}{10}$ permanganate oxidizes 6.3 grams of oxalic acid

and 1 c.c. of $\frac{\text{N}}{10}$ permanganate oxidizes 0.0063 gram of oxalic acid.

From these data calculate the percentage of oxalic acid in the crystalline substance.

Additional Exercises in Volumetric Analysis

1. To find the strength of a barium chloride, calcium chloride, or copper sulphate solution. Precipitate the metal as carbonate by a measured excess of normal sodium carbonate. Filter, wash, and titrate the excess of carbonate in the filtrate with normal acid.

2. To find the strength of a dilute bench alkali. Titrate with normal acid.

3. To find the strength of a solution of oxalic, acetic, citric or other organic acid. Titrate with normal sodium hydroxide, using phenolphthalein as indicator.

4. To estimate the purity of an ammonium salt. Dissolve a weighed quantity in water, add a measured excess of N. NaOH and boil till all ammonia has been expelled. Titrate the excess of NaOH with normal acid. An alternative method is to absorb the liberated ammonia in a measured excess of normal sulphuric acid, and titrate the excess with normal sodium hydroxide.

5. To determine the molecular weight of tartaric acid, the basicity being given; or given the molecular weight, to determine the basicity. Find by titration the equivalent weight and multiply by the basicity to get the molecular weight. To

determine the basicity divide molecular weight by equivalent weight.

6. To estimate the quantity of an oxalate in solution. Take a suitable weight, dissolve in water, add dilute sulphuric acid, heat to 60° and titrate the oxalic acid which is set free with $\frac{N}{10}$ permanganate.

7. To estimate the percentage of calcium in calcium carbonate. Weigh about 1.3 grams of dry calcium carbonate. Dissolve in dilute hydrochloric acid in a beaker. Warm and add an excess of ammonium oxalate, then make strongly alkaline with ammonia and boil. The calcium is precipitated as oxalate CaC_2O_4 . Filter and wash. Remove the paper from the funnel. Open it out and lay it on a clock glass, and wash every particle of precipitate into a beaker. Add a mixture of equal parts of sulphuric acid and water and warm till dissolved. Cool, and transfer to a 250 c.c. flask, make up to the mark and mix. Take 50 c.c. for titration with $\frac{N}{10}$ permanganate.

8. Lead may be estimated by the same method. Precipitate as oxalate, filter, dissolve the precipitate in dilute nitric acid and add sulphuric acid. Lead sulphate is precipitated, and oxalic acid is set free, which is titrated with $\frac{N}{10}$ permanganate without filtration.

9. To estimate the strength of hydrogen peroxide solution by titration with $\frac{N}{10}$ permanganate. The equation for the reaction is,



Take about 5 c.c. of 10 volume hydrogen peroxide and dilute to 250 c.c. in a graduated flask. Take 50 c.c. for titration, adding 20 c.c. of dilute sulphuric acid. Calculate the percentage strength.

QUESTIONS

1. Given a standard solution of sulphuric acid, containing 49 grams per litre, how could you ascertain the strength of a specimen of nitric acid? How could a standard acid such as the above be made? (Oxford and Camb. School Cert.)

2. A certain weight of sodium bicarbonate was heated to dull redness for about half an hour. The residue was then dissolved in water, and the solution made up to one litre. 500 c.c. of the solution were exactly neutralised by 45 c.c. of normal sulphuric acid. Find (a) the normality of the solution, and (b) the weight of sodium bicarbonate used. (Scot. Leaving Cert.)

3. Define the term 'normal solution,' using sulphuric acid and caustic soda to illustrate your answer. Why is sodium carbonate generally preferred to caustic soda, when making up a standard solution? Describe the preparation of normal sodium carbonate. 100 c.c. of dilute sulphuric acid required 80 c.c. of normal sodium carbonate for complete neutralisation. What weight of sulphuric acid did it contain? (Scot. Leaving Cert.)

4. What is a decinormal solution? Illustrate your answer by referring to sodium hydroxide and sodium carbonate. Describe fully the method you would employ to prepare a decinormal solution of hydrochloric acid. 15 c.c. of hydrochloric acid exactly neutralise 27 c.c. of a solution of sodium hydroxide. Calculate the number of grams of sodium hydroxide per litre of the solution. (Scot. Leaving Cert.)

5. If you were provided with a solution containing sodium chloride and hydrogen chloride, how would you find out the weights of these substances contained in a litre of the solution? Give full experimental details. (London Matric.)

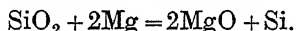
CHAPTER XXXII

SILICON. SILICA. GLASS

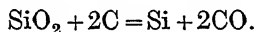
Silicon, symbol Si, atomic weight 28, is a non-metallic element which in its chemical behaviour resembles carbon.

Occurrence. Silicon is not found free in nature. Next to oxygen it is the most plentiful of all the elements, and forms a quarter of the crust of the earth. It is found as silicon dioxide or silica, SiO_2 , which is the most important constituent of rocks.

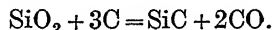
Preparation. Silicon may be prepared by heating a mixture of finely powdered magnesium and sand.



When the magnesium oxide is dissolved out with hydrochloric acid, silicon is left as a brown amorphous powder. Crystalline silicon is made on a large scale by heating a mixture of quartz and coke in an electric furnace.



If excess of carbon is used it unites with the silicon to form carborundum, SiC.



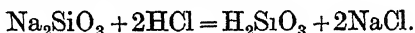
Prepared in this way, silicon is used for making alloys with iron, known by the general name of ferro-silicon, which are extremely resistant to corrosion by acids.

Silica. Silicon forms only one oxide, SiO_2 , silicon dioxide or Silica. Quartz or rock crystal is pure crystalline silica. When coloured by the presence of various metallic oxides it appears in the forms of topaz, amethyst, opal, agate and other beautiful and sometimes precious stones. Other forms of silica are flint and sand. Silica is much used for making chemical apparatus, crucibles, basins, combustion tubes, etc. Its advantages are: (1) It has a high melting point, about

1600°. (2) It is not attacked by acids. (3) It has a low coefficient of expansion. A silica vessel can be made red hot and plunged into cold water without cracking. A glass vessel treated in the same way would be shattered into small fragments. Quartz, melted in the oxy-hydrogen flame, can be drawn into threads which are frequently used for the suspension of parts of electrical instruments.

Silicic Acid. Silica is an acidic oxide and combines with bases to form salts known as silicates.

When hydrochloric acid is added to a solution of sodium silicate, a gelatinous substance is precipitated. The reaction may be represented by the equation,



This gelatinous substance is silicic acid, but there is a doubt as to whether it is a compound of definite composition. Silicic acid and its solution have no action on litmus and no acid taste; it has not therefore the usual properties of an acid. Theoretically there are two silicic acids, orthosilicic, H_4SiO_4 , and metasilicic, H_2SiO_3 , because the formulae of many well-known silicates show that they are derived from these acids.

Colloidal Substances. Silicic acid is one of a large class of substances known as **Colloids**. Thomas Graham (1861) divided dissolved substances into two classes, **Colloids** and **Crystalloids**, according as they diffused slowly or quickly in water.

If a dilute solution of sodium silicate is added to hydrochloric acid, there is no precipitation of silicic acid; it remains in 'colloidal' solution. It can be separated from the sodium chloride, which is a crystalloid, by **Dialysis**. The dialyser is a shallow dish without a bottom, in place of which a sheet of parchment is tied on. This vessel rests in a larger dish containing water to above the level of the parchment. The solution, containing silicic acid and sodium chloride, is poured into the dialyser and the apparatus allowed to stand. After some time the sodium chloride will have completely passed through the porous parchment, and a solution of silicic acid is left in the dialyser. This is a general method of separation of a colloid from a crystalloid. Some other colloidal substances are starch, gums, albumen, aluminium hydroxide. All soluble crystalline salts are crystalloids.



FIG. 100.—Dialyser.

Silicates. The only soluble silicates are those of sodium and potassium. Sodium silicate or 'water glass' is made as follows. Flint is heated to redness, quenched in water, ground to a fine powder and digested, under pressure, with sodium hydroxide. The product is a viscous liquid, and is used for fireproofing wood and other materials, for making artificial stone, for preserving eggs, etc.

Innumerable insoluble silicates are found in minerals and rocks. All clays are silicates of aluminium. From these, china, porcelain, earthenware, bricks, tiles and drain-pipes are made

Permutite. A double silicate of sodium and aluminium is used for softening water for boilers, under the name of 'permutite.' When hard water is passed through a layer of this substance, the calcium and magnesium displace the sodium, forming calcium and magnesium aluminium silicates; an equivalent quantity of sodium salts passes into the water. To re-activate the spent permutite, it is treated with brine, which displaces calcium and magnesium and restores the sodium.

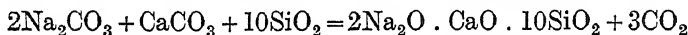
Expt.—The silica garden. A pretty experiment bearing this name shows the formation of metallic silicates. Fill a glass trough with a solution of sodium silicate, about 1.1 density, and drop into it crystals of nickel sulphate, copper sulphate, cobalt nitrate, zinc sulphate, ferrous sulphate and manganese sulphate. See that the crystals are well separated from one another. After standing for a day, plant-like growths begin to shoot up from the crystals, and the trough has the appearance of a miniature flower garden.

Glass. Glass is a mixture of silicates. The origin of this indispensable material may date back nearly 4000 years. Pliny says that the discovery of glass is due to some Phœnician sailors who had a cargo of soda or natron. They landed on the coast of Syria, and finding no stones on the shore to support their cooking pots, they used instead lumps of natron from their ship. To their surprise they found that the soda and sand had melted together under the heat of the fire and formed a transparent substance, glass. This may be only a legend, but we certainly know that glass-making was a flourishing industry in Egypt in 1500 B.C. The Romans learned the art from the Egyptians, and specimens of Roman glass preserved in the British Museum show that the workmen in these days were highly skilled.

It is said that in the reign of the Roman Emperor Tiberius a glass-maker invented a method of making malleable glass, and was invited by the Emperor to show him a specimen. He brought with him a vase which when thrown on the ground merely became dented, and could be hammered into shape again. In these days glass, on account of its fragility, was very valuable, so Tiberius asked him whether his secret was known to anybody else. On receiving the assurance that it was not, the Emperor ordered that he should be beheaded.

Afterwards Venice became the centre of the European glass-making industry, and the process was so much cheapened that glass soon came into general use. In 1850 a Venetian glass-maker introduced the manufacture into Britain.

Glass is a mixture of silicates. 'Soda lime glass' or 'soft glass' is made by melting together soda ash, limestone and sand. Only an approximate equation can be given, as each maker has his own 'formula' for glass-making mixtures.



Soft glass is easily fusible and is used for making window panes, bottles and tubing. If 'hard glass' is required, potassium carbonate is substituted for sodium carbonate. It has a higher melting-point and is suitable for flasks, beakers and combustion tubing. Another variety is 'potash lead glass.' This is made from potassium carbonate, lead oxide and sand. It is manufactured into glass ornaments, table glass, and cut glass. 'Optical glass,' from which lenses of cameras, microscopes and telescopes are made, is also a potash lead glass.

In addition to the common uses of glass already mentioned, it is to-day employed in many unusual ways, such as the making of houses, handbags, pearls, pavements, carpets and tapestry.

Tests for Silica and Silicates

1. Hydrochloric acid added to a solution of a soluble silicate gives a precipitate of silicic acid.

2. Make a small loop on the end of a piece of platinum wire. Moisten it and pick up a little powdered microcosmic salt, $\text{NaNH}_4\text{HPO}_4$. Heat in the flame till it melts and gives a transparent bead. If a minute quantity of a silicate is heated in this bead, the metallic oxide will dissolve and the silica will be left as a white skeleton.

Additional Experiments

EXPT.—Warm gently in a flask a mixture of calcium fluoride and sand with concentrated sulphuric acid. Pass the gaseous silicon fluoride into water. Filter and obtain gelatinous silicic acid.

EXPT.—Make a solution of water glass, and test the action upon it of litmus, carbon dioxide and hydrochloric acid.

EXPT.—Dialysis experiment. Put into the dialyser, starch solution mixed with potassium iodide. The potassium iodide diffuses into the water, and if tested with chlorine water gives the brown colour of dissolved iodine. The absence of a blue colour shows that no starch has passed through. If the starch in the dialyser be added the blue colour is at once produced.

QUESTIONS

1. Explain why carbon and silicon are regarded as being tetra-valent elements. Compare their oxides. How would you fully identify (a) a crystal of diamond, (b) a quartz crystal ?

(Oxford and Camb. School Cert.)

2. Describe the chemical and physical properties of the common crystalline forms of silica. How would you find the percentage of silica in a finely divided mixture of sand and black oxide of copper ?

(London Matric.)

3. How is glass made ? What are the chief kinds of glass used in chemical laboratories, and for what purposes are they used ?

(London Matric.)

CHAPTER XXXIII

PHOSPHORUS

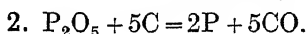
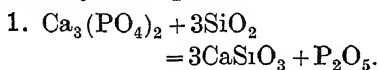
Phosphorus. Symbol P. Atomic weight 31. The name is derived from two Greek words, and means 'light-bearer.' Phosphorus is a non-metallic element and is usually classified with nitrogen, as many of their compounds have similar formulae, though their physical and chemical properties frequently differ widely.

Occurrence. The element cannot exist free in nature as it is so easily oxidized. It is found, however, in many minerals in combination with oxygen as phosphate, particularly as calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, and less frequently as ferric phosphate and aluminium phosphate. The bones of animals contain half their weight of calcium phosphate. When they are burned in air the organic matter is consumed and 'bone ash,' consisting mainly of calcium phosphate, is left.

History. Phosphorus glows in the dark when exposed to moist air. There are other substances which have the property of phosphorescence—for example, barium sulphide and calcium nitrate, and to these the name phosphorus or 'light-bearer' was originally applied. The substance we now call phosphorus was discovered by Brandt, a Hamburg alchemist, during his search for the Philosopher's Stone, and independently a few years afterwards by another German chemist, Johann Kunkel. Robert Boyle, after seeing specimens of Brandt's phosphorus, also succeeded in preparing it in 1680. The method used by all of them was the distillation of a mixture of sand and concentrated urine. In 1771 Scheele published a method of obtaining phosphorus from bone ash. Lavoisier showed that it was an element, and investigated some of its compounds.

Preparation. The chief source of phosphorus is calcium phosphate, either as the mineral, *rock phosphate*, or as *bone ash*. The raw material is powdered, mixed with coke and sand and

heated in an electric furnace. The mixture is fed through the hopper *A*, and carried by the Archimedean screw into the furnace, in which an arc is struck between two carbon electrodes, developing very intense heat. The silica displaces phosphorus pentoxide from the calcium phosphate to form calcium silicate, and the pentoxide is then reduced by the coke. The two stages are represented by the equations,



The phosphorus vapour and the carbon monoxide escape at the opening *C*, and the phosphorus is condensed by cooling in water. It is afterwards melted and cast into sticks, and is generally known as yellow phosphorus. Perfectly pure phosphorus, however, when not exposed to light is quite colourless and transparent.

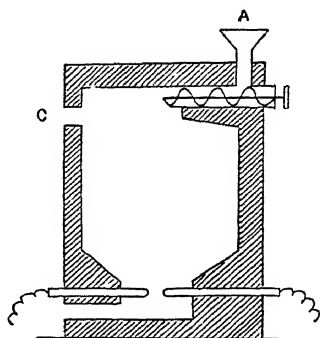


FIG 101.—Manufacture of Phosphorus

Properties of Phosphorus. The element exists in several allotropic forms, of which the most important are :

1. Yellow phosphorus, which is actually white, but becomes yellow on exposure to light.

2. Red phosphorus. This variety is not so chemically active as the yellow form. It is sometimes called amorphous phosphorus, but is in reality crystalline.

Yellow or Common Phosphorus. The density of the solid is 1.83. The vapour density is 62 and the molecular weight 124, so the vapour consists of P_4 molecules. Yellow phosphorus is a soft waxy solid which melts at 44° , and if exposed to air takes fire at a lower temperature, giving dense white fumes of phosphorus pentoxide, P_2O_5 . It causes painful burns which heal very slowly, and should always be handled with a tongs. It is easily cut with a knife, but this must be done under water, as the heat developed by the friction of cutting may cause it to ignite. Yellow phosphorus is insoluble in water, but is very soluble in carbon disulphide and to a less extent in turpentine and olive oil. When the solution in carbon

disulphide is evaporated slowly, the residue of finely divided phosphorus takes fire spontaneously. As we have already seen, the same thing happens when a filter paper is wetted with a few drops of the solution and dried. Common phosphorus is poisonous. It was formerly used in the manufacture of matches, but owing to the poisonous effects which followed the inhaling of its vapour, its use has been discontinued. Phosphorus glows in the dark; the phosphorescence is due to oxidation, as it does not glow in an inert gas, such as carbon dioxide or nitrogen. Ozone is a product of the oxidation of phosphorus, and its presence seems to be connected with phosphorescence, for substances like hydrogen sulphide and ethylene which destroy ozone prevent the glowing of phosphorus.

EXPT.—Place a little dry phosphorus in a flask and fill it up with glass wool. Pass a slow current of dry carbon dioxide through the flask while heating it on a water bath. The vapour of phosphorus carried by the gas oxidizes on coming in contact with the air, and a green flame appears at the top of the tube *A*. This is known as the 'cold flame,' and the hand may be held in it without injury.

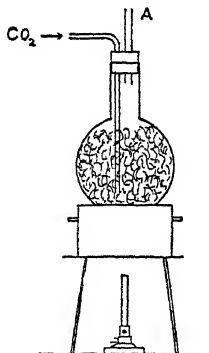


FIG. 102.

This experiment may be performed by the teacher.

Phosphorus takes fire when introduced into chlorine gas or brought in contact with solid iodine. With sulphur it unites directly at ordinary temperatures, giving sulphides of phosphorus. Nitric acid oxidizes it to phosphoric acid. The last two reactions are almost explosively violent and should be carried out with red phosphorus.

When yellow phosphorus is heated at 250° in absence of oxygen, it is converted into the allotropic modification, red phosphorus.

Red Phosphorus. Density 2.2. This is a dull red powder and is made by heating ordinary phosphorus for several days to 250° in an inert atmosphere of nitrogen or carbon dioxide. A trace of iodine helps the change catalytically. When yellow phosphorus is burned in air, a residue of red phosphorus may be observed. Red phosphorus has an ignition temperature of 240° , it is insoluble in carbon disulphide, does not readily

oxidize in air, does not show phosphorescence, and is not poisonous. It is the stable form of phosphorus. When the red variety is heated till it vaporises, it condenses on cooling to the yellow modification. This can be demonstrated by heating a small quantity of red phosphorus in a glass tube in a stream of carbon dioxide. The substance volatilises and condenses in colourless drops on the colder part of the tube. Both yellow and red phosphorus are finally oxidized on heating to phosphorus pentoxide, P_2O_5 .

Comparison of the properties of Yellow and Red Phosphorus.

	Yellow Phosphorus.	Red Phosphorus.
Colour	Pale yellow	Dull red
Smell	Distinctive	Odourless
Specific gravity	1.83	2.2
Ignition temperature	30°	240°
Action of air	Oxidation and phosphorescence	No action
Action of CS_2	Soluble	Insoluble
Caustic soda	Action	No action
Physiological action	Poisonous	Non-poisonous

Experiments with yellow phosphorus are attended with some risk on account of its extreme inflammability; very small quantities should be used, and it should not be touched with the fingers, as the heat of the hand is often sufficient to ignite it.

EXPTS.—1. Compare the colour, hardness and general appearance of the two varieties of phosphorus.

2. Place a small piece of yellow phosphorus in a test tube half full of water. Insert a thermometer, warm very gently and note the temperature at which it melts.

3. Test the solubility of yellow and red phosphorus in carbon disulphide.

4. To compare the ignition temperature of the two kinds of phosphorus. Touch a piece of yellow phosphorus with a knife blade which has been warmed by rubbing several times on the bench. Heat a small quantity of red phosphorus in a basin gently with a Bunsen flame.

5. Heat a little red phosphorus in a hard glass tube in a current of carbon dioxide, to show the transformation into the yellow variety.

Uses of Phosphorus. The principal use is in the manufacture of matches. The earliest matches, invented about

1805, were called 'oxymuriated' matches. These were splints of wood dipped into sulphur and afterwards tipped with a mixture of potassium chlorate, powdered sugar and gum. They ignited when dipped into a bottle of strong sulphuric acid—a very inconvenient thing to carry in the waistcoat pocket! John Walker, an English chemist, in 1826, invented the 'lucifer' match, which ignited when rubbed on a piece of sandpaper, and about 1835 a further improvement was introduced by the use of yellow phosphorus. The phosphorus match quickly displaced all others, but it was soon found that phosphorus vapour was extremely dangerous to workers, many of whom suffered from phosphorus disease, a decay of the jaw bones. After frequent attempts to regulate the industry, a law was finally passed prohibiting the use of yellow phosphorus for this purpose, and non-poisonous substitutes are now employed.

In match-making two kinds of substances are required. One is a substance which can be easily ignited by friction, the other is an oxidizing agent which supports the combustion long enough to enable the wood of the match to take fire. There are two general classes of matches, the ordinary match and the safety match. The former contains in its head the ignition substance, and strikes on any rough surface. The latter only strikes on the box, which has a prepared surface carrying the ignition substance. Yellow phosphorus was for many years used as the ignition substance. In its place phosphorus sesquisulphide, P_4S_3 , is now employed in the ordinary match head and red phosphorus on the safety match-box.

The match sticks are first dipped in paraffin for a quarter of an inch, and the tips are then dipped in the proper composition. For the head of the ordinary match the composition consists of phosphorus sesquisulphide, potassium chlorate, red lead, mixed with glue to bind the materials together. The safety match head is made of antimony sulphide, Sb_2S_3 , potassium chlorate and glue. The side of the box is coated with a mixture of red phosphorus, antimony sulphide, powdered glass (to assist friction) and glue.

Phosphine. Phosphorus forms compounds with hydrogen, or hydrides. The most important of these is Phosphine or Phosphoretted Hydrogen, which has the formula PH_3 .

Preparation of Phosphine. It is usually prepared by warming yellow phosphorus in a flask with strong caustic soda solu-

tion. As phosphine prepared in this way is spontaneously inflammable in air owing to the presence of a liquid hydride P_2H_4 , which has this property, the air in the flask must first be displaced by coal gas. The flask is then warmed, phosphine is evolved and passes through a delivery tube, the other end of which dips under water in a trough. The speed of evolution should be regulated to 1 hubble in 4.5 seconds, and each bubble as it meets the air takes fire, giving a white smoke ring of phosphorus pentoxide. The products are phosphine and sodium hypophosphite.

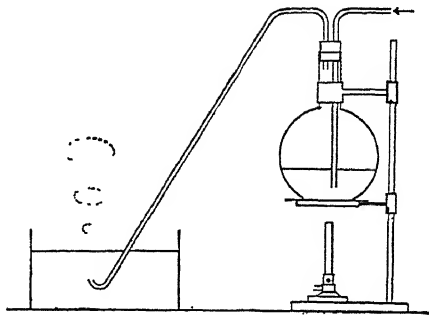
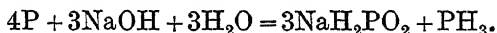
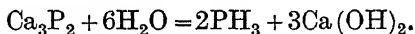


FIG 103

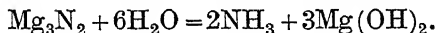


After the experiment is over and action has ceased, the delivery tube should not be removed until the phosphine has been completely driven out of the flask by coal gas, to avoid the risk of an explosion.

Another method of preparing phosphine is by the action of water on calcium phosphide, Ca_3P_2 .

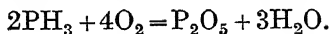


This resembles the action of water on magnesium nitride.

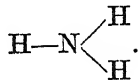
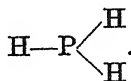


Phosphine prepared in this way is not spontaneously inflammable.

Properties. Phosphine is analogous to ammonia, and is feebly basic, uniting with dry hydriodic and hydrochloric acids to form 'phosphonium' salts. Phosphonium iodide has the formula PH_4I . Phosphine is a colourless gas with a disagreeable odour, slightly soluble in water and very poisonous. It is combustible, burning to phosphorus pentoxide and water.



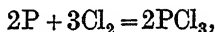
Comparison of the properties of Phosphine and Ammonia.



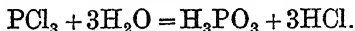
	Phosphine.	Ammonia
Physical state	- Colourless gas	Colourless gas
Smell	- Distinctive	Distinctive
Ignition point	- 100°	Non-inflammable
Solubility in water	- Slightly soluble	Very soluble
Aqueous solution	- Not alkaline	Strongly alkaline
Physiological action	- Poisonous	Non-poisonous

Chlorides of Phosphorus. Phosphorus trichloride, PCl_3 , and phosphorus pentachloride, PCl_5 .

The trichloride is prepared by passing dry chlorine over red phosphorus heated in a retort. Phosphorus trichloride distils over and is condensed in a cooled receiver. To convert the trichloride into the pentachloride, the former is allowed to drop slowly into a cooled flask through which a stream of chlorine is passing.



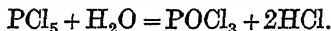
Phosphorus trichloride is a fuming liquid, decomposed by cold water into phosphorous acid and hydrochloric acid.



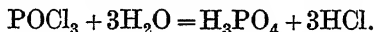
Phosphorus pentachloride is a yellow crystalline solid. It is dissociated on heating into the trichloride and chlorine,



which recombine on cooling. With a small quantity of water it gives phosphorus oxychloride, POCl_3 .



With an excess of water, phosphoric acid is formed.

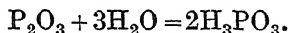


The chlorides of phosphorus are used in organic chemistry for replacing HO or hydroxyl groups by chlorine atoms.

Oxides of Phosphorus. We shall consider two of these, phosphorous oxide or phosphorus trioxide, P_2O_3 , and phosphoric oxide or phosphorus pentoxide, P_2O_5 . Vapour density

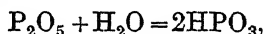
measurements show that the molecular formulae should be respectively, P_4O_6 and P_4O_{10} , but the formulae P_2O_3 and P_2O_5 and the names trioxide and pentoxide have become so firmly established by custom that they are still generally employed and are more convenient for use in equations.

Phosphorous Oxide, or Phosphorus Trioxide, P_2O_3 (P_4O_6). This oxide is formed, mixed with phosphoric oxide, when phosphorus is burned in a limited supply of air. It is a white crystalline solid which dissolves slowly in water, giving phosphorous acid.



Phosphorus trioxide is thus the anhydride of phosphorous acid.

Phosphoric Oxide, or Phosphorus Pentoxide, P_2O_5 (P_4O_{10}). This is obtained by burning phosphorus in air or oxygen. It is a white solid which readily absorbs moisture and is the best reagent for drying gases. It dissolves in water, forming first metaphosphoric acid,



which afterwards takes up more water, changing to orthophosphoric acid; the change is accelerated by boiling.



Phosphorus pentoxide is thus the anhydride of the phosphoric acids.

Observe carefully the use of the endings 'us' and 'ous.' The name of the element phosphorus always ends in 'us.' The termination 'ous' indicates a compound of a lower state of oxidation than the 'ic' compound. For example, phosphorus trichloride, phosphorus trioxide; but phosphorous oxide, phosphorous acid.

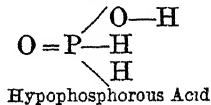
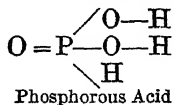
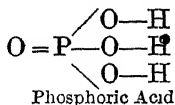
Acids of Phosphorus. There are three main acids, which are derived from different anhydrides.

Phosphoric acid, H_3PO_4 , from the anhydride, P_2O_5 .

Phosphorous acid, H_3PO_3 , from the anhydride, P_2O_3 .

Hypophosphorous acid, H_3PO_2 , from the hypothetical anhydride, P_2O .

These formulae may be written graphically, thus :



The hydrogen atoms replaceable by metals are those in the 'OH' groups. The molecule of phosphoric acid thus contains 3 replaceable hydrogen atoms and the acid is tribasic. That of phosphorous acid contains 2 replaceable hydrogen atoms and is dibasic, and hypophosphorous acid is monobasic as the molecule contains 1 atom of replaceable hydrogen. The formulae may also be written to shew the proportions of water and anhydride, $3\text{H}_2\text{O} \cdot \text{P}_2\text{O}_5$, $3\text{H}_2\text{O} \cdot \text{P}_2\text{O}_3$, and $3\text{H}_2\text{O} \cdot \text{P}_2\text{O}$.

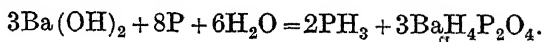
Phosphoric or orthophosphoric acid, H_3PO_4 , is formed by dissolving phosphorus pentoxide in water and boiling, or by boiling red phosphorus with nitric acid. It is a crystalline solid soluble in water and forms salts known as phosphates.

EXPT.—Ignite a piece of phosphorus on a glass plate under a bell jar. Collect the phosphorus pentoxide. Expose a small quantity to the air for some time, and observe whether any change takes place. Dissolve a little in water and test the solution with litmus paper. Dissolve about a gram in water and boil to convert metaphosphoric acid into orthophosphoric acid. Take part of the solution, make alkaline with ammonia, and add concentrated nitric acid till strongly acid. Then add ammonium molybdate solution in excess and warm. A yellow precipitate appears. This reaction is commonly used in the estimation of phosphorus. Take another portion of the solution, nearly neutralise (but do not make alkaline) with sodium hydroxide, and add silver nitrate solution. A yellow precipitate of silver phosphate comes down.

Phosphorous acid, H_3PO_3 , is formed when phosphorus trioxide is dissolved in water, and by the action of water on phosphorus trichloride. It is a white crystalline solid and forms salts called phosphites

EXPT.—Add a few drops of phosphorus trichloride to cold water to obtain a solution of phosphorous acid. This acid has reducing properties. Warm a little with mercuric chloride solution. The mercuric chloride is reduced to mercurous chloride and appears as a white precipitate. Silver nitrate is reduced to metallic silver, but the presence of ammonia is required to prevent the precipitation of silver chloride.

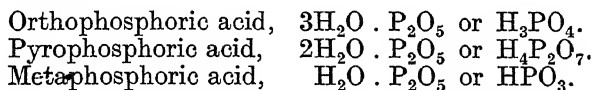
Hypophosphorous acid, H_3PO_2 , is made by boiling phosphorus with barium hydroxide solution, giving barium hypophosphite.



When the exact quantity of sulphuric acid is added to the solution, the barium is precipitated as sulphate and filtered

off. The filtrate contains a solution of hypophosphorous acid, from which the crystalline acid is obtained by evaporation and cooling. It forms salts called hypophosphites. The foregoing is a general method of isolating an acid. Hypophosphorous acid is more strongly reducing than phosphorous acid. It reduces mercuric chloride to metallic mercury. The hypophosphites of potassium, sodium, and calcium are used in medicine.

Phosphoric and phosphorous acids can exist in three forms, the *ortho*, *pyro*, and *meta* forms. These are, in the case of phosphoric acid,

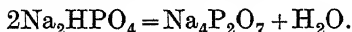


These form salts similarly named, orthophosphates, pyrophosphates, and metaphosphates.

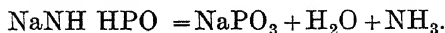
Meaning of the Prefixes, ortho, meta, and pyro. These are derived from Greek words meaning respectively, 'regular,' 'beyond, or less than the highest,' and 'fire.' When an anhydride forms more than one acid by uniting with different quantities of water, that containing the most water is called the *ortho* acid, one with less water is called the *meta* acid. These prefixes are also applied to salts of the acids. A *pyro* acid or salt is one which is derived from the *ortho* acid or salt by heating.

When orthophosphoric acid is heated it is converted with loss of water first into pyrophosphoric acid, and finally into metaphosphoric acid. Metaphosphoric acid is a transparent glassy solid and is frequently called 'glacial' phosphoric acid.

The ordinary laboratory sodium phosphate has the formula Na_2HPO_4 . It is a crystalline salt containing 12 molecules of water of crystallisation, which it loses on heating. On stronger heating sodium pyrophosphate is formed.

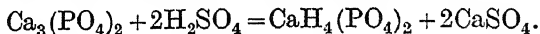


If hot solutions of sodium phosphate and ammonium chloride be mixed and crystallised, a double phosphate with the formula $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ crystallises out. This is known as microcosmic salt. On heating, it is converted into sodium metaphosphate, NaPO_3 .



Sodium metaphosphate dissolves metallic oxides, some of which impart to it distinctive colours, used as a test for metals.

Phosphorus is required by man for the building up of bone and the development of muscular and nerve tissue. Man obtains it from plants, which derive it from calcium phosphate in the soil. Calcium phosphate can only be absorbed by plants when in solution, and as it is not very soluble, it is necessary in using it as a fertiliser to convert it into a more soluble form. This is done by treatment with sulphuric acid, which changes it into 'acid phosphate' or 'superphosphate.'



Superphosphate is a well-known commercial fertiliser; others containing phosphorus are *bone ash*, and *basic slag* from steel furnaces.

Additional Experiments

EXPT.—In the dark, lower a piece of luminous phosphorus into a jar containing a few c.c. of ether. Note disappearance of luminosity.

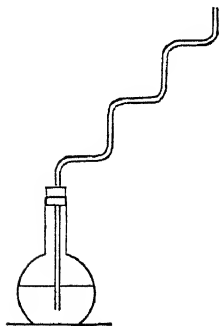


FIG 104.

EXPT.—Place a piece of yellow phosphorus in silver nitrate solution and another piece in copper sulphate solution. Allow to stand for some days. Observe the formation of phosphides.

EXPT.—Formation of phosphorus pentachloride. Fill a flask with well-dried chlorine. Place a small piece of yellow phosphorus in a deflagrating spoon, the stem of which passes through the cork of the flask, and lower into the chlorine.

EXPT.—Another method of demonstrating the phosphorus glow. Boil a piece of phosphorus in water in a flask fitted with a tube bent as shown in the diagram.

QUESTIONS

1. Write a short note on one of the following: (1) manufacture of phosphorus, (2) refrigeration by means of ammonia, (3) manufacture of coal gas for domestic purposes. (Scot. Leaving Cert.)

2. How may yellow phosphorus be converted into the red variety and red phosphorus into the yellow form? State clearly

the principal properties of these two forms of the element, and give an account of the uses to which they are applied.

(London Matric.)

3. Describe briefly the compounds which hydrogen forms with nitrogen and phosphorus, and give the most important methods by which they are obtained. Compare their properties.

(Oxford and Camb. School Cert.)

4. Describe the preparation of (*a*) phosphorus trichloride, and (*b*) phosphine. Shew how the latter is related to ammonia.

(London Matric.)

5. Name four substances which can be employed in drying gases. Explain why each substance is used for this purpose, and state which are suitable and which are unsuitable for drying (*a*) ammonia, (*b*) hydrogen chloride, (*c*) carbon dioxide, and (*d*) hydrogen sulphide, giving the reason in each case.

(London Matric.)

6. Write an account of the oxides and chlorides of phosphorus, and mention some purposes for which they are used. Explain the changes produced by heating (*a*) ordinary sodium phosphate, and (*b*) microcosmic salt.

(Oxford and Camb. School Cert.)

7. Write a clear explanatory note on each of the following: (*a*) the use of calcium carbide in cycle lamps, (*b*) the ingredients of gunpowder, (*c*) the fact that safety matches strike on the box only.

(Scot. Leaving Cert.)

CHAPTER XXXIV

PROPERTIES OF THE COMMON GASES

IN closing the section dealing with the non-metals, it may be of assistance to our memories to have a summary of those properties of the common gases upon which their identification and separation depend.

Oxygen. Colourless and odourless. Supports combustion. No action on litmus. Mixed with nitric oxide gives brown fumes. Mixed with twice its volume of hydrogen and exploded, gives water. Passed over heated copper gives copper oxide. Absorbed from a mixture of gases by shaking up with an alkaline solution of pyrogalllic acid. Carbon dioxide and other acid gases are also absorbed by the alkali and must first be removed.

Ozone. Colourless. Characteristic odour. Shaken in a flask with mercury causes the mercury to adhere to the glass. Bleaches indigo. Liberates iodine from potassium iodide. Oxidizes black lead sulphide to white lead sulphate.

Hydrogen. Colourless and odourless. Inflammable. Flame held against a cold surface deposits water. No action on litmus. Reduces copper oxide, giving copper and water; no carbon dioxide. Carbon monoxide and methane also reduce copper oxide, but give carbon dioxide. Estimated in a mixture of gases, after removing other combustible gases, by explosion with excess of oxygen.

Carbon Dioxide. Colourless and odourless. Non-inflammable. Does not support combustion. Slight acid action on litmus. Turns lime water milky. Decomposed by burning magnesium with separation of carbon. Absorbed from a mixture of gases by sodium hydroxide. Other acid gases are also absorbed.

Carbon Monoxide. Colourless and odourless. Inflammable. Non-supporter of combustion. No action on litmus. Reduces

copper oxide, giving copper and carbon dioxide. Absorbed by a solution of cuprous chloride in hydrochloric acid.

Methane. Colourless and odourless. Inflammable. Non-supporter of combustion. No action on litmus. Reduces copper oxide, giving copper, carbon dioxide and water.

Nitrogen. Colourless and odourless. Non-inflammable. Non-supporter of combustion. No action on litmus. No simple direct test is available. The only common gas which may be mistaken for nitrogen is carbon dioxide, and it can be identified as already explained.

Nitrous Oxide. Colourless. Odour and taste generally described as 'sweet.' Non-inflammable. Supporter of combustion, but not quite so effective as oxygen. Distinction from oxygen: not absorbed by pyrogallic acid, no brown fumes with nitric oxide.

Nitric Oxide. Colourless. On exposure to air gives brown fumes of peroxide. Non-inflammable. Non-supporter of combustion.

Suppose you are given three jars, containing respectively oxygen, nitrous oxide and nitric oxide. How can they be distinguished?

1. Transfer a little gas from each jar to a test tube under water, and expose to air. The tube which shows brown fumes must contain nitric oxide. Call this jar *A*.

2. Take a little of the contents of jars *C* and *D* in test tubes and add to each some gas from jar *A*. The one which shows brown fumes must contain oxygen, and the other nitrous oxide.

Nitrogen Peroxide. Colour reddish brown. Has a distinctive odour. Non-inflammable. Supports combustion of very strongly burning substances. Acid to litmus. Absorbed by sodium hydroxide. Make solution acid with sulphuric acid and apply the brown ring test for nitrate.

Ammonia. Colourless. Ammoniacal odour. Non-inflammable. Alkaline to litmus. Gas gives white fumes with hydrogen chloride. Its solution added to copper sulphate gives a dark blue colour.

Chlorine. Colour greenish yellow. Characteristic odour. Non-inflammable. Wax taper burns in it with a smoky flame. Filter paper wetted with turpentine takes fire. Bleaches litmus. Displaces iodine from potassium iodide.

Hydrogen Chloride. Colourless. Pungent irritating odour. Compare with that of sulphur dioxide. Non-inflammable.

Does not support combustion. Acid to litmus. White fumes with ammonia. Solution dissolves metals—for example, zinc and magnesium—and gives a white precipitate with silver nitrate.

Hydrogen Sulphide. Colourless. Odour of rotten eggs. Inflammable. Flame held against a cold basin gives a yellow stain of sulphur. Non-supporter of combustion. Slightly acid to litmus. Reacts with sulphur dioxide, setting free sulphur. Blackens lead acetate paper. Solution reduces acidified potassium permanganate and potassium dichromate. Decolorises iodine solution. Precipitates metallic sulphides.

Sulphur Dioxide. Colourless. Choking odour of burning sulphur. Acid to litmus. Mixed with hydrogen sulphide sets free sulphur. Reducing action same as hydrogen sulphide.

QUESTIONS

1. The members of the following pairs are sometimes mistaken for one another. State the points of resemblance in each case, and give two tests by which you would distinguish one from the other.

- (a) hydrogen and carbon monoxide,
- (b) sulphur dioxide and hydrogen chloride,
- (c) nitrous oxide and oxygen,
- (d) nitrogen and carbon dioxide. (Scot. Leaving Cert.)

2. If you had a jar of gas given you, how could you tell whether it contained chlorine, oxygen, hydrogen, carbon monoxide, carbon dioxide, or ammonia? (London Matric.)

3. Describe and explain at least three experiments in which chemical action takes place between gases at the ordinary temperature of the air. (London Matric.)

4. Name all the oxides which are gases at the temperature of the atmosphere, and describe how each is prepared. (London Matric.)

5. Allocate the common gases to the following classes: (a) combustible gases, (b) gases soluble in water, (c) coloured gases, (d) inert gases. Describe the properties of one example selected from group (c).

6. Arrange the following gases in the ascending order of their densities, and indicate which are less dense and which are denser than air: ammonia, carbon monoxide, chlorine, hydrogen chloride, methane, nitric oxide, oxygen, sulphur dioxide, hydrogen sulphide. ($H=1$; $C=12$; $N=14$; $O=16$; $S=32$; $Cl=35.5$.)

(Scot. Univ. Entrance)

CHAPTER XXXV

SODIUM AND POTASSIUM

It has been already stated that the chemical elements can be divided into two classes, non-metals and metals, and the chief differences between these have been discussed in Chap. XVI. Our study has so far been confined to the non-metals, and we will now consider a few representatives of the metallic class.

Sodium. Symbol Na. Atomic weight 23. Melting point 96° . Specific gravity 0.97. The symbol Na is derived from the Latin *natrium*. Sodium and potassium are members of the group known as *alkali* metals because some of their compounds received the name *alkalies* long before the metal was known.

Occurrence. Sodium is never found in the elementary state in nature. Only the less easily oxidizable metals such as gold, platinum, silver, and copper, can exist free. Iron and nickel are also found in meteorites.

The most abundant natural compound of sodium is sodium chloride or common salt, the sources of which have been mentioned in Chap. XXVI. Sodium nitrate is found in rainless desert districts in Peru and Chile. Sodium carbonate exists in soda lakes in East Africa and California. Sodium compounds enter into the composition of many silicate rocks and are very widely distributed.

Extraction of the Metal. In 1807 Sir Humphry Davy discovered that sodium was an element; prior to his time the caustic alkalies were supposed to be elements. He prepared the metal by the electrolysis of fused caustic soda, and it is still made in the same way by the Castner process.

The Castner Process. Caustic soda is fused in an iron pot *A*. The iron cathode *B* rises through the bottom of the pot and is surrounded by a cylindrical nickel anode *C*, from which it is separated by a wire gauze. Hydrogen and sodium are liberated

at the cathode and collect in the vessel *D*, the hydrogen preserving the sodium from oxidation. Oxygen comes off at the anode and escapes through the pipe *E*.

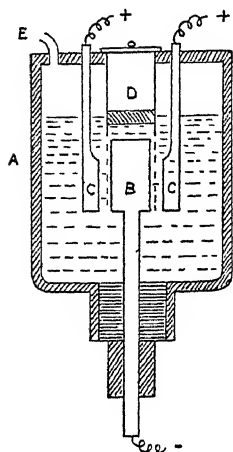


FIG 105 —Manufacture of Sodium

Both oxygen and hydrogen are collected

Sodium is also made by the electrolysis of fused sodium chloride

Properties of Sodium. When freshly cut it shows a silvery white surface, which on exposure to air speedily becomes covered with a film of oxide. It must, therefore, be kept under naphtha or petroleum. Sodium is soft and light, burning in air with a golden yellow flame to sodium peroxide, Na_2O_2 , and reacting vigorously with water, giving sodium hydroxide and hydrogen.

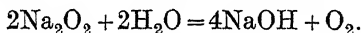
EXPT.—Cut a piece of sodium with a knife and observe its softness, its silvery appearance, and the quick formation of a film of oxide. *N.B.*—*You already know the action of water on sodium, so do not handle it with wet fingers.* Heat a piece of

sodium strongly in a metal spoon to find whether it burns.

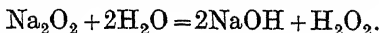
Compounds of Sodium. There are two oxides.

Sodium Monoxide, Na_2O , is obtained, mixed with peroxide, by burning sodium in a limited supply of air.

Sodium Peroxide, Na_2O_2 , is formed when the metal is burned in excess of air or oxygen. It is a yellowish powder, decomposed by water with evolution of oxygen,

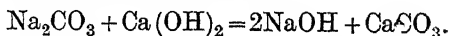


Sodium peroxide is a powerful oxidizing agent, and is used for bleaching, as with *cold* water it gives hydrogen peroxide.



Sodium Hydroxide, or caustic soda, NaOH .

1. Caustic soda may be prepared by boiling a dilute solution of sodium carbonate with lime,



Calcium carbonate is precipitated. The clear solution, after filtration, is evaporated and the caustic soda is fused in

iron pots and cast into sticks or sold in the form of coarse powder.

2. The electrolysis of brine. The Castner-Kellner cell has been described in Chap. XXVI. Another and different form is the Hargreaves-Bird cell. In the first process the sodium travelling to the cathode is carried by mercury into the inner cell, where it meets water and becomes sodium hydroxide. In the Hargreaves-Bird cell the sodium ions pass through a cell wall of asbestos into an outer cell containing the cathode, where they give up their electric charges and react with steam to form caustic soda. The asbestos cell wall or diaphragm is permeable by ions, but not by the brine molecules.

3. Electrolysis of fused sodium chloride. In this process molten lead is used as the cathode, in which the sodium set free dissolves, forming an alloy. This is afterwards decomposed by steam, giving sodium hydroxide and hydrogen.

Properties. Caustic soda is a white crystalline solid. When exposed to air it absorbs moisture and deliquesces, but the solution gradually solidifies again owing to absorption of carbon dioxide. It dissolves readily in water, giving out much heat. Its solution is strongly alkaline. Caustic soda has a powerful corrosive action on the skin, slowly attacks glass, and dissolves zinc and aluminium. It readily absorbs carbon dioxide and sulphur dioxide, and is used to separate these from gas mixtures. The hydroxides and carbonates of sodium and potassium are sometimes called *fixed* alkalis to distinguish them from the *volatile* alkali ammonia.

Uses. Sodium hydroxide has many uses as a reagent in the laboratory, in the precipitation of metallic hydroxides, as an absorbent in gas analysis, and as a standard solution in volumetric analysis. In industry, it is used extensively for soap-making, dyeing, paper-making, and in the manufacture of artificial silk.

EXPT.—Mix 10 grams of quicklime with water in a porcelain basin, and add to it 5 grams of anhydrous sodium carbonate, dissolved in 100 c.c. of water. Boil for 10 minutes. Allow to settle. Pour off 2-3 c.c. of clear liquid into a test tube and add hydrochloric acid. Continue heating until this test shows no effervescence, indicating that the sodium carbonate has been all converted into hydroxide. Let the liquid cool, and filter.

EXPT.—Test the liquid prepared in the last experiment with litmus paper. Add a little to solutions of the following salts in a

test tube, and note the colour of the precipitates: chromium sulphate, ferric alum, nickel sulphate, cobalt nitrate, copper sulphate, and mercuric chloride. Repeat these experiments with the bench sodium hydroxide.

Sodium hydroxide added to a solution of a metallic salt gives a precipitate of the hydroxide of the metal, if it is insoluble. Write equations for the above reactions

EXPT.—Test the action of strong caustic soda solution on zinc and aluminium.

Sodium Carbonate, or Soda, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. This is the most important compound of sodium. Sodium and potassium carbonates are known as *mild* alkalies to distinguish them from the *caustic* alkalies or hydroxides.

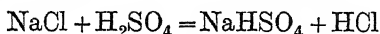
History. Alkaline substances were known to the Arabian chemists, to whom we owe the name alkali. See potassium In the eighteenth century sodium carbonate and potassium carbonate were first recognised as different substances. Sodium carbonate or *barilla* was mainly derived from the ash obtained by burning seaweed and potassium carbonate from wood ash. Sodium carbonate was also introduced into Europe from Africa by the Arabs, and it is still found naturally occurring in soda lakes in British East Africa

As the manufacture of soap, glass, and other substances requiring an alkali increased, the demand for sodium carbonate exceeded the supply from natural sources, and chemists began to consider the possibility of making soda from common salt, of which a cheap and inexhaustible supply could be obtained. In 1775 the French Academy of Science offered a large prize to the discoverer of a process for making soda from salt. This was won by Nicolas Leblanc, and he established a factory in 1791, which worked for some years quite satisfactorily. The process was on the same lines as the present-day one which still bears his name. However, Leblanc never received his prize. During the French Revolution his factory was confiscated, and unable to bear the burden of poverty and despair, he committed suicide in 1806. About eighty years later a tardy acknowledgement of his services to chemical industry was made by the erection of a statue to his memory. His process was worked in England in the early part of the nineteenth century by Muspratt, and at St. Rollox in Glasgow by Tennant.

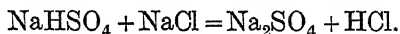
Manufacture of Sodium Carbonate

1. **The Leblanc Process.** The production of soda by this process reached its peak sixty years ago, and since then has steadily dwindled. Were it not for the recovery of the valuable by-products hydrochloric acid and sulphur, it would long ago have been extinct, but it is still worked on a small scale. The method has been supplanted by the Ammonia Soda or Solvay process, and there are signs that it in its turn may have to give way to Electrolytic Soda. As the Leblanc process is instructive, a short account of it may be given.

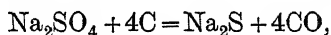
The raw material, common salt, is heated with sulphuric acid. The first action is the production of acid sodium sulphate.



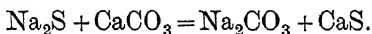
On heating to a higher temperature, normal sodium sulphate is formed.



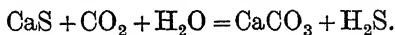
The sodium sulphate, or *saltcake*, is mixed with coal and limestone and heated strongly in a cylindrical revolving furnace. The reaction may be represented by two equations. The sulphate is first reduced by the carbon to sulphide,



and this reacts with the limestone, giving sodium carbonate and calcium sulphide,



The product is known as *black ash*, and consists of sodium carbonate, calcium sulphide, lime, coal, and other substances. It is crushed and treated with water to dissolve the sodium carbonate. The solution is evaporated till the soda crystallises out as $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, or 'washing soda.' The residue left is *alkali waste*, and contains sulphur in calcium sulphide. It is mixed with water, and a stream of carbon dioxide is blown through, when the following reaction takes place,

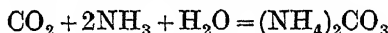


The hydrogen sulphide is then burned with insufficient air for complete combustion, and sulphur is set free.

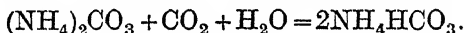
This sulphur recovery method is known as the Claus and Chance process.

2. The Ammonia Soda or Solvay Process. This process, though known earlier, was first successfully worked on a commercial scale by Solvay, a Belgian chemist, in 1865. It depends on the fact that when ammonium bicarbonate is added to a strong solution of sodium chloride, sodium bicarbonate is precipitated.

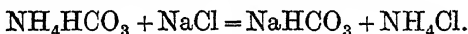
In practice, pure brine is first saturated with ammonia and allowed to trickle down towers which are fitted with perforated shelves. Carbon dioxide is blown in at the base of the tower and meets the descending stream of ammoniacal brine. The following reactions take place. Carbon dioxide, ammonia and water unite to form ammonium carbonate,



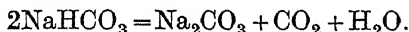
Further action of carbon dioxide gives ammonium bicarbonate,



The ammonium bicarbonate then reacts with brine to form sodium bicarbonate and ammonium chloride,



Sodium bicarbonate is precipitated, withdrawn at the bottom of the tower, and separated from the ammonium chloride by means of a vacuum filter. It is then heated to about 270° in a furnace, and anhydrous normal sodium carbonate or *soda ash* is obtained,

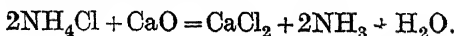


The soda ash is dissolved in water and crystallised, giving washing soda, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.

A little study will show that this is an economical process. It is a good example of the utilisation of by-products. The carbon dioxide is in the first place obtained by heating limestone,



The carbon dioxide is used in the process and is recovered by the final heating of sodium bicarbonate to soda ash, and used again. The lime is employed in treating the ammonium chloride to recover ammonia,



The ammonia goes back to saturate the brine, so the only waste product is calcium chloride, CaCl_2 .

3. Electrolytic Soda. Electrolytic caustic soda is treated with carbon dioxide. Sodium bicarbonate is precipitated, filtered, and heated to obtain *soda ash*. This process is making steady headway, and with cheaper electric current, will probably in time displace all others.

The industries of a country naturally gravitate towards districts where a plentiful supply of fuel and raw material is available, to save cost of transport, which is one of the heaviest burdens. The alkali industry has for this reason become centred in Cheshire and Lancashire, where salt, coal and limestone are found in abundance. Other examples are the manufacture of iron and the production of aluminium. The former is carried on in proximity to the coal and iron ore deposits of Yorkshire, Staffordshire, South Wales and Lanarkshire, and the latter, which depends on electrical power, has gone to Kinlochleven and Foyers in Scotland, where water power is available for generating electric current.

Properties of Sodium Carbonate. It forms large transparent crystals containing 10 molecules of water of crystallisation. When exposed to air it effloresces, becoming coated with a layer of the monohydrate, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$. Sodium carbonate is readily soluble in water, and its solution has an alkaline reaction. It is used in the manufacture of glass, soap, paper and many other substances.

Sodium Bicarbonate, or Baking Soda, NaHCO_3 . This is a white crystalline substance, giving a solution with a very slight alkaline reaction. It can be made by the action of carbon dioxide on the normal carbonate. On heating it loses carbon dioxide, reverting to the normal carbonate. Sodium bicarbonate is used in baking bread, which is aerated by the carbon dioxide set free. See p. 138. Doctors frequently prescribe it as a corrective of stomach acidity.

Sodium Chloride, NaCl . See Chaps. XXVI-XXVII.

Sodium Bromide and Sodium Iodide resemble the corresponding potassium salts, which are of greater importance and are described in the following chapter.

Sodium Sulphate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. This is known as Glauber's salt, and crystallises from its solution below 32° with 10 molecules of water. If the solution be crystallised above that temperature it deposits crystals of anhydrous sulphate. The anhydrous form is more soluble in water than the hydrated form, as may be seen from the diagram of

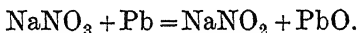
solubilities on p. 15. On exposure to air the decahydrate effloresces, losing its 10 molecules of water and turning into the anhydrous salt, Na_2SO_4 .

Sodium sulphate is made commercially as *saltcake* by the Leblanc process. It can also be obtained by neutralising sodium hydroxide with sulphuric acid.

Sodium Thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. See p. 268.

Sodium Nitrate, NaNO_3 , is found naturally in Chile, in beds which lie close to the surface of the ground. They are mined, and the nitre rock or *caliche* is crushed and extracted with water. From the solution, sodium nitrate is crystallised out. The mother liquor contains sodium iodate, one of the main sources of iodine. Sodium nitrate is a white crystalline deliquescent salt. It is used in the manufacture of nitric acid and as a fertiliser. See p. 197.

Sodium Nitrite, NaNO_2 , is made by heating sodium nitrate with lead.



It is a faintly yellow crystalline solid, and is used in the manufacture of aniline dyes.

Tests for Sodium. The Flame Test is a characteristic test for sodium and several other metals whose compounds impart colour to a non-luminous Bunsen flame.

EXPT.—Pour 2-3 c.c. of concentrated hydrochloric acid into a watch glass. Dip into it the tip of a platinum wire and pick up a minute fragment of the powdered substance. Hold it in the outer mantle of the flame. After each test clean the wire carefully by alternately dipping in hydrochloric acid and heating, till it gives no colour to the flame. Experiment with a salt of each of the following metals; a chloride or nitrate is best.

Metal.	Colour.
Sodium.	Yellow.
Potassium.	Violet (best viewed through a cobalt blue glass).
Lithium.	Crimson.
Strontium.	Crimson.
Calcium.	Red (rather fugitive).
Barium.	Green.
Copper.	Green or blue.
Lead	Light blue.
Arsenic }	
Antimony }	

Potassium

Potassium. Symbol K. Atomic weight 39.1. Melting point 62° . Specific gravity 0.87.

History. The Arab chemists prepared impure potassium carbonate from wood ashes and called the substance obtained *al kali*, meaning the ash. From *kali* is derived the Latin *kalium*, the first letter of which is used as the symbol of potassium. Later, wood alkali was called *potash*, as in its preparation it was calcined in pots, and from potash comes the name potassium. Sir Humphry Davy isolated the metal at the same time as sodium, and in the same way. See p. 303.

Occurrence. Potassium compounds are widely distributed in nature, but are found in much smaller quantity than those of sodium. Granitic rocks contain *felspar*, $K_2O \cdot Al_2O_3 \cdot 6SiO_2$. When these are disintegrated and decomposed by the action of frost, water, oxygen, and carbon dioxide, the potassium compounds are washed into the soil, from which they are absorbed by plants. For the last seventy years the chief source of potassium compounds has been the great salt beds at Stassfurt in Germany. They contain chlorides and sulphates of sodium, potassium, magnesium, and calcium. The compound from which potassium is mainly obtained is *carnallite*, $KCl \cdot MgCl_2 \cdot 6H_2O$. In more recently worked saline deposits in Alsatia and Galicia, potassium chloride, KCl, is found as *sylvine*.

Preparation of Potassium. The method is the same as that used in the preparation of sodium. See p. 303.

Properties. Potassium is a soft silvery metal with a bluish tinge, and is more chemically active than sodium. It oxidizes more readily and decomposes water more violently. The liberated hydrogen takes fire, burning with a lilac-coloured flame.

Compounds of Potassium. The metal is monovalent in all its compounds, which much resemble those of sodium.

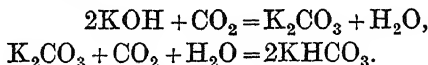
Oxides. There are two oxides, K_2O and K_2O_4 . The latter is formed when potassium burns in oxygen. They both dissolve in water, giving the hydroxide.

Potassium Hydroxide, or caustic potash, KOH, is made in the same way as sodium hydroxide and is similar in properties.

Potassium Carbonate, K_2CO_3 , can be manufactured by the Leblanc process. See p. 307. It cannot, however, be made by

the Solvay process, as the bicarbonate is much more soluble and is not precipitated like the sodium compound.

Potassium Bicarbonate, KHCO_3 , is obtained by passing carbon dioxide through a strong solution of the normal carbonate or hydroxide.



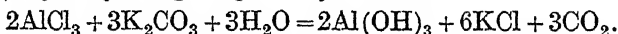
Potassium Chloride, KCl , is extracted from *carnallite* or *sylvine* by crystallisation. May be made by the action of hydrochloric acid on the hydroxide or carbonate.

Potassium Bromide, KBr , and Potassium Iodide, KI . These salts are prepared by warming bromine or iodine with iron filings to obtain the bromide or iodide of iron, which may be represented by the simplest formulae, FeBr_3 and FeI_3 . These are dissolved in water and heated with potassium carbonate, which precipitates ferric hydroxide. This is filtered off, and the filtrate contains potassium bromide or iodide, which is separated by crystallisation.

Observe that potassium carbonate precipitates ferric hydroxide, not ferric carbonate. When sodium or potassium carbonate solution is added to a solution of a metallic salt, the carbonate of the metal is generally precipitated. Sometimes, however, the carbonate is partly or completely hydrolysed, especially on boiling. Thus we get a number of basic carbonates by partial hydrolysis.

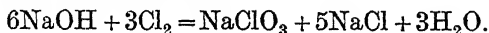


The carbonates of iron, aluminium and chromium are completely hydrolysed, giving the hydroxides.



Potassium bromide and iodide are both white crystalline salts, and are used in photography and in medicine.

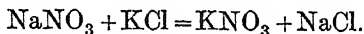
Potassium Chlorate, KClO_3 . Potassium chlorate is made commercially by the electrolysis of hot brine. The chlorine produced at the anode is allowed to react with the sodium hydroxide which is formed at the cathode. This gives sodium chlorate and sodium chloride.



The solution is then treated with potassium chloride. It then contains four possible salts, potassium chloride and chlorate,

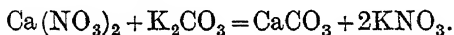
sodium chloride and chlorate. Potassium chlorate is the most insoluble of these, and therefore crystallises out first on evaporation. It is a white crystalline salt of which 100 c.c. of water dissolves about 7 grams at 20°. See also p. 232.

Potassium Nitrate, KNO_3 , is also called *nitre* and *saltpetre*. It is usually manufactured from sodium nitrate or Chile salt-petre by the addition of potassium chloride to a hot solution.

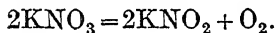


Sodium chloride is the most insoluble combination, and can be crystallised out first, leaving a solution of potassium nitrate which is then evaporated and crystallised.

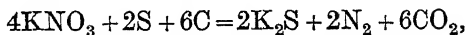
Calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, is made in India by the oxidation of nitrogenous animal refuse in the soil through the agency of bacteria in the presence of lime or calcium carbonate. The calcium nitrate is dissolved out with water and treated with wood ashes (containing potassium carbonate). Calcium is precipitated as carbonate, and potassium nitrate is recovered from the filtrate on evaporation.



Potassium nitrate is a white crystalline salt very soluble in water. On heating it melts and is gradually decomposed into potassium nitrite and oxygen,



It is used in making gunpowder, a mixture of 6 parts of potassium nitrate, 1 part of charcoal, and 1 part of sulphur. The reason of the explosive properties of gunpowder is that a large volume of gas is produced when the materials react together, so that when it is ignited in a closed space the pressure of the gas has a powerful disruptive effect. The action may be given by the equation,



but various other compounds are formed at the same time. Newer and more powerful explosives have displaced gunpowder in many of its uses, but it is still to some extent employed in blasting.

Potassium Nitrite, KNO_2 , is made by heating potassium nitrate.

Potassium Sulphate, K_2SO_4 , is an anhydrous salt. It is found in the Stassfurt beds, and is separated by fractional crystallisation. It is a very useful fertiliser for grain crops.

EXPTS.—Perform the same experiments with potassium as with sodium, using the same precautions.

Tests for Potassium

1. The flame test has already been described on p. 310.
2. Add a little tartaric acid solution to a concentrated solution of a potassium salt; a white crystalline precipitate of potassium hydrogen tartrate comes down. Rubbing the side of the test tube with a glass rod hastens precipitation.
3. To 5 c.c. of a strong solution of potassium chloride add an equal bulk of alcohol, then a few drops of a solution of platinic chloride. Warm gently and rub the test tube with a glass rod, a yellow precipitate comes down.

QUESTIONS

1. Describe a process for making sodium carbonate from common salt. How is sodium hydroxide made on the large scale ?
(Oxford and Camb. School Cert.)
2. How would you prepare a small quantity of sodium hydrogen carbonate, if you were supplied with chalk, sodium, hydrochloric acid and water ? Draw the apparatus you would use. How would you shew that the product obtained is not washing soda ?
(London Matric.)
3. What is the composition of washing soda ? What takes place when it is (a) freely exposed to air, (b) added to permanently hard water containing calcium sulphate, (c) strongly heated with silica, (d) dissolved in a little water and the solution saturated with carbon dioxide.
(London Matric.)
4. Give a brief account of electrolytic (or other) methods used for the manufacture of (a) caustic soda, (b) metallic sodium, (c) chlorine.
(Oxford and Camb. School Cert.)
5. Explain the use of washing soda for softening water. Why do washing soda crystals, on exposure to the air, gradually change to a white powder ? It was found that 5 grams of the crystals required 35 c.c. of normal hydrochloric acid for neutralisation, and that 5 grams of the white powder required 80.6 c.c. of normal hydrochloric acid for neutralisation. Determine (a) the number of

molecules of water of crystallisation in washing soda crystals and
(b) the percentage of anhydrous sodium carbonate in the white powder.
(Scot. Leaving Cert.)

6. What are by-products in a chemical reaction ? Illustrate your answer by reference to the formation and importance of by-products encountered in some manufacturing process with which you are familiar.
(Scot. Univ. Entrance.)

7. From what sources and by what processes may caustic potash, potassium carbonate and bicarbonate be obtained ?
(Oxford and Camb. School Cert.)

8. 'Potassium chlorate is a crystalline solid, more soluble in hot than in cold water ; when heated it decomposes, giving off oxygen, and leaving a substance which contains chlorine ; when hot it is a strong oxidizing agent.' How would you show by experiments that these statements are true ?
(London Matric.)

CHAPTER XXXVI

MAGNESIUM AND CALCIUM

Magnesium. Symbol Mg. Atomic weight 24.32. Melting point 632° . Specific gravity 1.74.

History. *Magnesia*, or magnesium oxide, and magnesium carbonate seem to have been known at a very early date, but were often confused with other allied substances. Their composition was first made clear by Joseph Black in 1755, in his paper on *magnesia alba* and *quicklime*, in which he showed that *magnesia* and lime were distinct substances. See calcium. *Magnesia alba* was the name given to a basic magnesium carbonate which by 1700 was an article of commerce. About the same time a salt which had medicinal properties was obtained from the mineral springs of Epsom and was called 'Epsom salt.' This is magnesium sulphate. In 1808 Sir Humphry Davy isolated impure metallic magnesium by electrolysis.

Occurrence. The chief naturally occurring compound of magnesium is the carbonate, MgCO_3 , which is found as *magnesite*, and in a double carbonate of magnesium and calcium named *dolomite*, $\text{MgCO}_3 \cdot \text{CaCO}_3$. It also occurs as sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, in *Epsom salts*, as magnesium chloride, MgCl_2 , and sulphate, MgSO_4 , in salt deposits. *Asbestos*, *talc*, *serpentine*, and other minerals also contain magnesium.

Extraction. The metal is obtained by the electrolysis of the fused chloride.

Properties of Magnesium. It is light, silvery white in colour, and does not oxidize in dry air. In moist air it becomes tarnished with oxide. It is readily soluble in dilute acids. When heated, it burns with a brilliant white light rich in actinic rays, which is used in 'flash-light' photography. Magnesium is a powerful reducing agent. It burns in steam and carbon dioxide, forming magnesium oxide, and reduces many metallic oxides on heating.

Uses. Magnesium is used in small quantities in some light and strong alloys. Two of the most important of these are *magnalium* and *duralumin*, the first consisting of magnesium and aluminium and the latter containing in addition a little copper and manganese. These alloys are chiefly used in the construction of air-ships and aeroplanes.

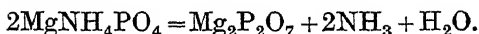
Compounds of Magnesium. It is divalent in its compounds

Magnesium Oxide or Magnesia, MgO , is produced, along with some nitride, Mg_3N_2 , when magnesium is burned in air. It may also be obtained by heating the carbonate or nitrate. It is a white powder which is slightly soluble in water and combines with it to form the hydroxide, giving the solution an alkaline reaction. Magnesia has a very high melting point, about 2000° , and is consequently used for making 'refractory' bricks to line furnaces. It is also employed in medicine.

Magnesium Hydroxide, $Mg(OH)_2$. On adding the hydroxide of sodium, potassium, or ammonium to a solution of a magnesium salt, a white precipitate of magnesium hydroxide comes down. This is soluble in acids and in ammonium chloride.

Magnesium Carbonate, $MgCO_3$, is found naturally as *magnesite*. The precipitate obtained by adding sodium carbonate to a solution of a magnesium salt is a basic carbonate. The composition of *magnesia alba* is $3MgCO_3 \cdot Mg(OH)_2$.

Magnesium Ammonium Phosphate, $MgNH_4PO_4 \cdot 6H_2O$ This substance is obtained as a white crystalline precipitate when sodium phosphate is added to a solution of a magnesium salt made strongly alkaline with ammonia. On filtration and heating, it is decomposed into magnesium pyrophosphate, ammonia and water.



This reaction is used in the estimation of magnesium.

Tests for Magnesium

1. When a magnesium compound is heated on a charcoal block by the blowpipe, moistened with cobalt nitrate solution and reheated, the residue has a pink colour.

2. Add sodium phosphate solution to a solution of magnesium sulphate containing half its bulk of ammonia. A white precipitate of magnesium ammonium phosphate comes down.

Calcium

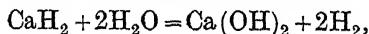
Calcium. Symbol Ca. Atomic weight 40. Melting point 780° . Specific gravity 1.52. Calcium is one of a typical chemical family of three elements, calcium, strontium, and barium. These are known as the alkaline earth metals, and their properties and those of their compounds resemble each other closely.

History. The name calcium is derived from the Latin *calx*, meaning 'lime.' The metal was first prepared by Davy in 1808, by electrolysis, but compounds of calcium derived from limestone have been known from very early times.

Occurrence. Calcium carbonate is found in enormous quantities as crystalline *marble*, and amorphous *limestone* and *chalk*. Other crystalline forms are *calcite*, *Iceland spar* and *aragonite*. Many great mountain ranges consist entirely of *limestone*, *marble* or *dolomite*, the double carbonate of calcium and magnesium. Chalk is composed of the shells of minute marine organisms deposited on the ocean bed and raised afterwards by earth upheavals. Calcium is also found as sulphate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, in *gypsum* and *alabaster*, as phosphate, $\text{Ca}_3(\text{PO}_4)_2$, in *apatite*, and as fluoride, CaF_2 , in *fluorspar*, a mineral which exists in a variety of beautiful colourings.

Preparation of Calcium. It is prepared by the electrolysis of the fused chloride. The metal attaches itself to the iron cathode which dips into the bath, and is gradually raised, carrying with it a stick of metallic calcium.

Properties of Calcium. When newly cut it is a bright silvery metal, rather harder than lead. It oxidizes in air, burns when heated, and decomposes water. When heated in nitrogen it gives calcium nitride, Ca_3N_2 , and heated in hydrogen forms a hydride, CaH_2 , known as *hydrolith*, a grey powder. This substance acts upon water, giving hydrogen,



and is used as a ready method of obtaining the gas. Observe that the quantity of hydrogen set free is twice that contained in the hydrolith.

Compounds of Calcium. It is divalent in its compounds.

Calcium Oxide or Quicklime, CaO , is made by heating the carbonate or nitrate. When treated with water it is transformed into calcium hydroxide or *slaked lime*, $\text{Ca}(\text{OH})_2$, with evolution of heat. See p. 145.

Calcium Hydroxide or Slaked Lime. This substance is a caustic alkali. It is fairly soluble in water, giving an alkaline solution known as lime water. It is frequently used technically when a cheap alkali is required. See p. 145.

Calcium Carbonate, CaCO_3 . is found in nature as already described. Calcium also forms an acid carbonate or bicarbonate, $\text{Ca}(\text{HCO}_3)_2$. The relationship between these compounds has been discussed in Chap. XIX.

Stalactites and Stalagmites. These remarkable and often beautiful formations are the result of the decomposition of calcium bicarbonate. When water containing this compound in solution drips from the roof of a cave it loses some carbon dioxide, and calcium carbonate is deposited. Thus, crystalline growths are slowly formed which hang from the roof like icicles, and are called *stalactites*. When the drop falls to the ground, the same action takes place. In this case the growth builds upwards, and is called a *stalagmite*.

Black's Researches. Joseph Black, who was Professor of Chemistry in the University of Edinburgh from 1766-1799, published in 1755 an important paper entitled *Experiments upon Magnesia alba, Quicklime, and Other Substances*.

The early chemists believed that the mild alkalis (carbonates) and the caustic alkalis (hydroxides) were elementary substances. Their properties were already known, and their reactions were interpreted in terms of the *phlogiston* theory. See p. 28. Phlogiston was considered to be the 'Principle' of fire and of causticity (burning). Limestone when burned was supposed to absorb phlogiston, which gave quicklime its caustic properties.

Limestone + Phlogiston = Quicklime.

When sodium carbonate is boiled with lime, calcium carbonate and caustic soda are formed. See p. 304.

Mild alkali + Phlogiston = Caustic alkali.

The phlogiston was supposed to be transferred to the caustic soda.

Black applied the test of the balance, and obtained the following results. When chalk is converted into quicklime, there is loss of weight due to the escape of a gas which Black called 'fixed air' (carbon dioxide) and the quicklime produced neutralises exactly the same amount of acid as the

original chalk. 'Fixed air' is also given off by the action of acids on mild alkalies and chalk. Chalk gives the same amount of 'air,' whether it is treated with acid or heated in a furnace. Quicklime can be changed again into chalk by boiling with a mild alkali, and the weight produced is the same as that of the original chalk. Black therefore concluded that chalk is a compound of quicklime with fixed air (carbon dioxide), and that the mild alkalies are also compounds of fixed air with other substances resembling quicklime. He also showed that the oxide and carbonate of magnesium, while resembling those of calcium, are distinct substances.

Calcium Sulphate is found naturally occurring as *gypsum*, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and *anhydrite*, CaSO_4 . On heating to about 120° gypsum loses part of its water, and is then known as Plaster of Paris. When mixed with water it recombines with it and sets to a hard mass. It is used as a cement and for making casts.

Calcium Phosphate, $\text{Ca}_3(\text{PO}_4)_2$, Calcium Carbide, CaC_2 , and Bleaching Powder, CaOCl_2 , have already been discussed.

EXPT.—Examine as many different forms of calcium carbonate, calcium sulphate and calcium fluoride as are available.

EXPT.—Wrap a piece of marble round with iron wire, or place on a sheet of iron gauze, and heat at the highest possible temperature. When cold, slake with water. Observe crumbling and rise of temperature. Test with litmus paper.

EXPT.—Heat powdered gypsum at a temperature between 120° and 130° . Cool, and mix with water. Lay aside and notice whether it sets hard. If heated above 130° it will not set.

EXPT.—Use of bleaching powder as an oxidizing agent. To solutions of lead nitrate and manganous sulphate add caustic soda, obtaining a precipitate of the hydroxide. Then add bleaching powder solution, which oxidizes the hydroxide to dioxide.

Tests for Calcium Salts

1. With solutions of calcium salts ammonium carbonate gives a white precipitate.
2. Ammonium oxalate gives a white precipitate.
3. Calcium compounds moistened with hydrochloric acid give a brick red colour to the Bunsen flame.

QUESTIONS

1. Give the names of the rock and mineral forms of (a) calcium carbonate, (b) calcium sulphate. What products are formed when calcium carbonate is heated, and to what use are they put in industry ?

2. What is Plaster of Paris, and how is it prepared ? What change takes place in the 'setting' of Plaster of Paris ?

(Scot. Univ. Entrance.)

3. What is the difference between 'mild' alkalies and 'caustic' alkalies ? Give a short account of Black's investigation of the nature of these substances.

CHAPTER XXXVII

COPPER

Copper. Symbol Cu. Atomic weight 63.6. Specific gravity 8.9. Melting point 1083°

History. Copper was one of the first metals used by man, probably because it is found naturally in the metallic state. After the Stone Age came a Copper Age, when the metal was employed throughout Europe for ornaments and implements, until the discovery of bronze, an alloy of copper and tin, introduced the Bronze Age. In the British Museum there is a copper pin which was found in an Egyptian tomb, and is perhaps the oldest metal implement known. Its age is estimated at about 10,000 years. The Romans obtained copper from Cyprus and called it *aes cyprum*, afterwards shortened to *cuprum*, from which is derived the symbol Cu. The alchemists associated the metals known to them with the names and symbols of the sun and the planets. Thus, gold, silver, mercury, tin, lead and iron were called Sun, Moon, Mercury, Jupiter, Saturn, and Mars. The name of copper was Venus, and its symbol was ♀.

Occurrence. Copper is found in the native state in the Lake Superior district of North America and in Chile and Bolivia in South America. The principal ore is *copper pyrites* or *chalcopyrite*, CuFeS_2 or $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$. Cuprous sulphide, Cu_2S , occurs as *copper glance* or *chalcocite*. Copper is also found as oxide in *red copper ore* or *cuprite*, Cu_2O , and as a basic carbonate in *malachite*, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, a beautiful green stone used for ornamental purposes. Copper ores are found in most parts of the world. The principal producing country is the U.S.A., Japan and Chile come second and third.

Smelting Metallic Ores. Metals are frequently obtained by mixing the oxide with carbon in the form of coke, and heating the mixture in a blast furnace—that is, a furnace through which a blast of air is blown to obtain as high a temperature as

possible. The process is known as **Smelting**. Metallic ores are seldom quite pure; they generally contain a quantity of earthy matter which must be separated from the metal. This is done by the addition of a **Flux**, which unites with the earthy material, forming a fusible mixture of silicates called **Slag**. The slag, being lighter, floats on top of the molten metal, and does not mix with it. As we know, basic oxides do not unite with acidic oxides, nor do acidic oxides unite with basic oxides. A basic oxide requires an acidic oxide, and *vice versa*. Therefore, if the earthy matter in the ore is acidic, consisting mainly of silica, a basic flux such as limestone is needed. If the earthy matter or *gangue* (pronounced gang) is basic, an acidic flux like silica or sand is required.

Sulphide ores are not easily reduced by carbon or carbon monoxide, as carbon has little attraction for sulphur, so they are usually roasted to convert them into oxides.

Extraction of Copper from Copper Pyrites

1. **Roasting.** The ore is first roasted to drive off part of the sulphur as sulphur dioxide. It is not desired in this case to get rid of all the sulphur and convert the metals into oxides. Copper pyrites contains both copper and iron, and if the mixed oxides were reduced to metal in the blast furnace an alloy of copper and iron would be obtained, which is not wanted. The aim of the process is to oxidize the iron and separate it in the form of slag without oxidizing the copper.

Roasting is usually done in a vertical furnace containing a series of shelves which are heated by a gas flame or by hot-air flues. The ore is charged on to the topmost shelf and is mechanically worked along by rakes till it drops on to the second shelf. It is raked again till it falls on to the third, and so on, until it arrives at the bottom, when the roasting is complete. The arrangement of shelving in one type of furnace is shown in the diagram.

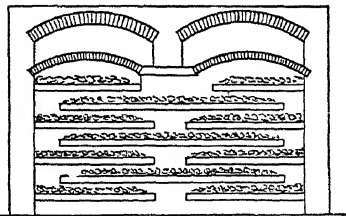


FIG. 106.—Delplace Roasting Furnace.

2. **Smelting.** The roasted ore, which contains oxides and sulphides of copper and iron, is mixed with sand and a little

coke and smelted in a blast furnace. The iron oxide combines with the silica to form a ferrous silicate slag, and the iron is thus partly got rid of. Metallic copper is not obtained (as already explained) but a dark grey metal known as *Matte*, which consists of a mixture of cuprous and ferrous sulphides containing about 45% of copper.

3. *Bessemerizing*. The molten matte is then poured into a Bessemer converter, a barrel-shaped furnace somewhat resembling the steel converter. See p. 348. A flux is added, and a blast of air is blown through the metal which oxidizes the iron and sulphur, but does not oxidize the copper. The iron oxide unites with the flux to form slag, and the sulphur is volatilised as sulphur dioxide. The iron is thus finally separated from the copper.

4. *Electrolytic Refining*. The crude copper from the Bessemer converter is usually refined by electrolysis. It is cast into blocks which form the anodes, the cathodes consisting of thin sheets of pure copper. These are immersed in acidified copper sulphate solution. All the anodes are connected in parallel with the positive source of current, and all the cathodes similarly connected with the negative source.

The copper sulphate ionises into $\text{Cu}^{++} + \text{SO}_4^{--}$. When the current is switched on, the copper ions are deposited on the cathodes, the SO_4^{--} ions attack the anodes, forming copper sulphate, which keeps up the strength of the bath. The net result is that copper travels from the anode to the cathode. Impurities either dissolve in the bath or are deposited on the bottom of the bath as anode mud. From this mud, gold and silver are recovered.

Properties of Copper. Copper has a characteristic red colour. It is very malleable and ductile, and an excellent conductor of electricity. It does not oxidize in pure dry air, but on exposure to moist air it tarnishes, and finally becomes covered with a green coating of *verdigris*, a basic carbonate.

Hydrochloric acid and dilute sulphuric acid have little action on copper. Concentrated hot sulphuric acid dissolves it (p. 254). Dilute nitric acid gives copper nitrate and nitric oxide (p. 192). Strong nitric acid gives copper nitrate and mainly nitrogen peroxide (p. 199). Copper is displaced from its salts in solution by zinc, iron, and aluminium.

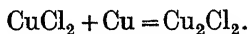
Uses of Copper. After iron, copper is the most useful of the metals. On account of its high conductivity and resistance to

corrosion, it is used extensively in the electrical industries. With other metals it forms alloys of great commercial importance. Brass contains 70% of copper and 30% of zinc. Bronze and gun-metal have about 90% of copper and 10% of tin. Aluminium bronze has about 95% of copper and 5% of aluminium. German silver or nickel silver contains 60% of copper, 20% of zinc and 20% of nickel.

Copper forms two series of compounds; cuprous, in which the metal is monovalent, and cupric, in which it is divalent.

Cuprous Compounds. **Cuprous Oxide**, Cu_2O , occurs naturally as *cuprite*. It is a red solid insoluble in water. When copper is heated in air a scale forms upon it composed of black cupric oxide on the outside and red cuprous oxide next the metal. Cuprous oxide is usually prepared by the reduction of *Fehling's* solution. This is a blue liquid containing 10 grams of sodium hydroxide, 35 grams of sodium potassium tartrate and 7 grams of copper sulphate dissolved in water and made up to 100 c.c. The solution is brought to the boil and glucose is added gradually. The copper sulphate is reduced to cuprous oxide, which comes down as a red precipitate. This reaction is made use of in the estimation of sugars. Cuprous oxide is oxidized to cupric oxide on heating in air.

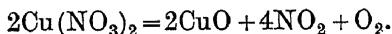
Cuprous Chloride, Cu_2Cl_2 , is obtained by boiling a solution of cupric chloride, CuCl_2 , with copper turnings and hydrochloric acid till colourless.



When the liquid is poured into a large excess of water, a white precipitate of cuprous chloride appears. When copper is heated in chlorine cuprous chloride, and not cupric chloride, is obtained, as the latter breaks up readily into cuprous chloride and chlorine (p. 216). Cuprous chloride is a white crystalline powder insoluble in water but soluble in strong hydrochloric acid and ammonia. These solutions are used for the absorption of carbon monoxide from a mixture of gases.

Cuprous Sulphide, Cu_2S , is found in nature as *chalcocite* (the *ch* is pronounced as 'k'). It can be made by heating copper with sulphur.

Cupric Compounds. **Cupric Oxide**, CuO , is made by heating copper in air or oxygen and by heating cupric nitrate.



It is a black substance, much used in the analysis of organic compounds, as it oxidizes carbon to carbon dioxide, and hydrogen to water, both of which are absorbed and weighed.

Cupric Hydroxide, $\text{Cu}(\text{OH})_2$, is a blue substance, precipitated from solutions of cupric salts by sodium hydroxide. Cupric hydroxide is soluble in ammonia, giving a deep blue liquid which dissolves cellulose, and is used in the manufacture of artificial silk. Cotton or wood pulp is dissolved in the solution, which is then forced through very minute holes into a bath of sulphuric acid, where it hardens into fine threads. This is known as the *cuprammonium* process, but has been largely replaced by another, called the *viscose* process.

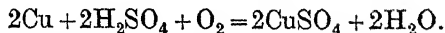
Cupric Chloride, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, is obtained in the form of green crystals by dissolving cupric oxide, hydroxide, or carbonate in hydrochloric acid and evaporating.

Cupric Carbonate. When sodium carbonate solution is added to a solution of a cupric salt, a blue precipitate comes down. This is a basic carbonate which may have the formula $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$. The normal carbonate CuCO_3 is unknown.

Cupric Sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, or *bluestone*, can be prepared by dissolving cupric oxide, hydroxide, or carbonate in dilute sulphuric acid and crystallising, or by heating copper in concentrated sulphuric acid (p. 254).



It is made commercially by heating copper with dilute sulphuric acid and blowing air through the liquid.



When $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is heated, it loses its water of crystallisation and becomes anhydrous copper sulphate, CuSO_4 , a white salt which turns blue on addition of water, reverting to the hydrated form. Copper sulphate is used in dyeing, in copper-plating, as an insecticide and as a germicide for spraying potatoes, vines, etc.

Cupric Sulphide, CuS , is obtained as a black precipitate on passing hydrogen sulphide through a cupric solution.

Tests for Copper

1. Dip a piece of iron or zinc in copper sulphate solution. It receives a coating of copper.

2. Copper compounds moistened with hydrochloric acid colour the gas flame green.

3. Hydrogen sulphide gives a black precipitate of cupric sulphide, CuS .

4. Sodium hydroxide gives a blue precipitate.

5. Ammonium hydroxide in excess gives a deep blue solution.

6. Potassium ferrocyanide gives a brown precipitate of copper ferrocyanide, $\text{Cu}_2\text{Fe}(\text{CN})_6$.

QUESTIONS

1. Write a short note on the occurrence of copper in nature. Give an account of any method employed of obtaining the metal from the ore, noting particularly any points in which your knowledge of science enables you to understand the processes.

(Scot. Leaving Cert.)

2. Describe the oxides of copper. Suppose 2.37 grams of cupric oxide to be completely reduced by heating in hydrogen, calculate the weights of metal and of water which would be obtained. ($\text{Cu} = 63.6$; $\text{O} = 16$; $\text{H} = 1$.) (Oxford and Camb. School Cert.)

3. Describe in outline any method for the preparation of copper from its ores. How would you prepare from metallic copper the cuprous and cupric oxides and chlorides ?

(Oxford and Camb. School Cert.)

4. Starting with ordinary precipitated copper carbonate, describe how you would prepare (a) cupric oxide, (b) metallic copper, (c) hydrated copper sulphate, and (d) pure dry carbon dioxide. (London Matric.)

CHAPTER XXXVIII

ZINC AND MERCURY

Zinc. Symbol Zn. Atomic weight 65.37. Melting point 419°. Specific gravity 7.

History. Brass, an alloy of copper and zinc, was in use long before the metal zinc was known, but the term 'brass' as used in the Old Testament was probably applied to any alloy containing copper, and possibly to copper itself. Zinc is first mentioned in the fifteenth century by Basil Valentine, who may have given it its name. In 1721 Henckel invented a process for the extraction of zinc from *calamine*, and the manufacture of the metal was established in England in 1740.

Occurrence. The chief ores of zinc are the sulphide, ZnS , in *zinc blende*, the carbonate, ZnCO_3 , in *calamine*, and the oxide, ZnO , in *red zinc ore*. Zinc oxide is white, but the mineral is coloured red by oxides of iron and manganese.

Extraction. The ore is first roasted to obtain the oxide. The roasted ore is then mixed with powdered coal and placed in fireclay retorts, which are heated by means of producer gas. The retorts must be heated to over 1200°, as this is the temperature at which zinc oxide is reduced by carbon. Zinc boils at 930°, so on reduction it is volatilised and passes from the retorts as zinc vapour, which is condensed in fireclay receivers. Commercial zinc is known as *spelter*.

Properties of Zinc. It is a bluish white metal, crystalline and brittle. On heating to 100°-150° it becomes malleable and ductile. Dry air does not affect it, but the combined influence of air, moisture, and carbon dioxide lead to the formation of a coating of basic carbonate which then protects the metal. When strongly heated, zinc burns, giving the oxide.

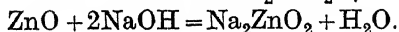
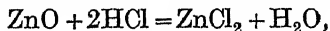
Ordinary commercial zinc dissolves readily in acids and more slowly in caustic alkalies. Acids have little action on a chemically pure metal. Corrosion, and the solution of metals in acids, are electrolytic processes: numerous electrolytic cells

are formed by the metal, the acid, and the impurities, thus accelerating solution. Consequently the fewer the impurities, the slower is the solvent action of the acid. If pure zinc be placed in dilute sulphuric acid it does not readily dissolve, but if a few drops of copper sulphate be added, solution takes place immediately. Zinc displaces copper from copper sulphate, just as iron does; the zinc acts as the anode, the sulphuric acid as the electrolyte, and the copper as the cathode. The result is that zinc goes into solution.

Uses of Zinc. It is largely used for making so-called 'galvanised' iron, on account of its resistance to corrosion. Sheet iron is cleaned in acid and scoured with sand. It is then dipped into molten zinc, a little tin being sometimes added to give the surface a crystalline or 'spangled' appearance. Afterwards it is bent into the familiar 'corrugated' iron. Other methods of coating with zinc are, Electrodeposition, the Schoop process, and Sherardising. In the Schoop process, the metal is coated by means of a fine spray of molten zinc; in Sherardising it is packed in zinc dust and heated. Many alloys contain a proportion of zinc. Two of the most important of these, brass and German silver, have already been mentioned.

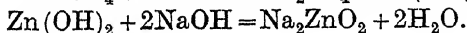
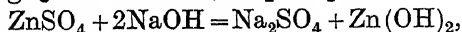
Compounds of Zinc. It is divalent in its compounds.

Zinc Oxide, ZnO , is produced by heating the metal, the carbonate or the nitrate. It is a white powder insoluble in water, and is used as a paint under the name of zinc white. White lead, the most widely used white paint, blackens on exposure to air owing to the formation of black lead sulphide. Zinc sulphide is white, so zinc white does not change colour. Zinc oxide dissolves in acids, forming zinc salts. It is an *amphoteric* oxide, and also dissolves in alkalis, giving compounds in which the zinc is in the acid radical.



Zinc oxide is also used in the manufacture of linoleum, as a glaze for pottery, and in soaps and ointments.

Zinc Hydroxide, Zn(OH)_2 . When sodium hydroxide is added to a solution of a zinc salt, a white precipitate of zinc hydroxide is obtained, which redissolves on adding more alkali, forming sodium zincate, Na_2ZnO_2 .



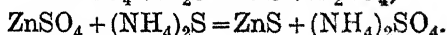
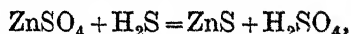
Zinc Chloride, ZnCl_2 , can be prepared anhydrous by heating zinc in hydrochloric acid gas. Hydrated zinc chloride is made by dissolving zinc in hydrochloric acid. Its solution dissolves paper and cotton, and is a powerful caustic. The soluble zinc compounds are poisonous.

Zinc Sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, or white vitriol, is isomorphous with magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. It is made on a large scale by roasting zinc blende with excess of air to obtain the sulphate and dissolving in water.

Zinc Nitrate, $\text{Zn}(\text{NO}_3)_2$, is made by dissolving zinc in nitric acid. The chloride, sulphate, and nitrate are all soluble salts.

Zinc Carbonate, ZnCO_3 , is made by adding sodium *bicarbonate* to a solution of a zinc salt. *Normal* sodium carbonate gives a precipitate of *basic* zinc carbonate.

Zinc Sulphide, ZnS , is partly precipitated on passing hydrogen sulphide through a neutral solution of a zinc salt. Acid is set free in the reaction, which prevents complete precipitation, as the sulphide is soluble in acids.



Ammonium sulphide or hydrogen sulphide + ammonia precipitates the sulphide completely by neutralising the acid formed.

Tests for Zinc

1. Add sodium hydroxide to a solution of zinc sulphate. Note white precipitate soluble in excess.

2. Add ammonia solution to zinc sulphate solution. To another portion of zinc sulphate solution add ammonium chloride, then ammonia.

3. Pass hydrogen sulphide through zinc sulphate solution for some time. Filter off precipitate. Make the filtrate alkaline with ammonia.

4. Heat a little zinc sulphate on a charcoal block with the blowpipe. Moisten with cobalt nitrate and reheat. Observe, green colour of residue.

Mercury

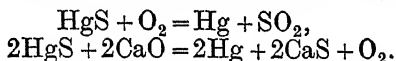
Mercury. Symbol Hg. Atomic weight 200.6. Boiling point 360° . Specific gravity 13.6.

History. The extraction of mercury from *cinnabar* is such a simple matter, that we are not surprised that the metal has

been known from a very early period. The mines at Almaden in Spain have probably been worked from 600 B.C. Mercury was regarded by the ancients as a perfect metal on account of its unchanging brightness, and the Arab chemists, as we have already seen, held the theory that all metals were composed of mercury and sulphur. The Greeks called it 'liquid silver,' from which is derived the Latin word *hydrargyrum* and the symbol Hg. It received its name from Mercury, the messenger of the gods, whose wand was used as its symbol, ☿. The old English name is quicksilver.

Occurrence. Mercury is found free in small quantities. The chief ore is *cinnabar*, the sulphide, HgS , which is found in Spain, Mexico, Peru, Japan, and elsewhere.

Extraction. Cinnabar is roasted to oxidize the sulphur, liberating the metal. It is also sometimes heated with lime



The mercury comes off as vapour and is condensed in chambers or in pear-shaped vessels called *aludels*, which fit into each other in a row. It may be purified by distillation or treatment with dilute nitric acid, which dissolves metallic impurities.



FIG 107—Aludels.

Properties of Mercury. It is a silvery white liquid, freezing at -39° and boiling at 360° . It is unchanged in air at ordinary temperatures, but on heating for some time at 350° it is gradually converted into the red oxide, HgO , which is decomposed below a red heat. Mercury is not acted on by hydrochloric acid, almost unaffected by dilute sulphuric acid, but dissolved by hot strong sulphuric acid.



It is dissolved by cold dilute nitric acid, giving mercurous nitrate, HgNO_3 , and by hot strong nitric acid, giving mercuric nitrate, $\text{Hg}(\text{NO}_3)_2$.

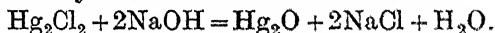
Uses of Mercury. It is used in the extraction of gold and silver from their ores, as it combines with these metals to form an alloy or *amalgam*. It is also employed in the manufacture of *vermilion*, in silvering mirrors, in making thermometers, and in the laboratory for the collection of gases.

Amalgams. Mercury alloys with many metals, and these alloys are called *amalgams*. Sodium and potassium amalgams are made by adding the metal in small pieces to warm mercury. They are decomposed by water, giving the alkaline hydroxide and hydrogen, and are often used as reducing agents. Many amalgams are plastic, setting slowly to a hard mass, a property which makes them useful in dentistry for stopping teeth; these may contain tin, gold, and other metals. Note that the term *amalgam* is only applied to alloys of mercury.

Compounds of Mercury. Mercury forms two series of salts: mercurous, in which the metal is monovalent, and mercuric, in which it is divalent. The soluble salts of mercury are poisonous.

Mercurous Compounds

Mercurous Oxide, Hg_2O , is a dark brown powder obtained by adding sodium hydroxide to mercurous chloride.



On heating, it decomposes into mercuric oxide and mercury.

Mercurous Chloride, Hg_2Cl_2 , also known as *calomel*, comes down as a white precipitate when sodium chloride is added to mercurous nitrate solution. It is made commercially by heating a mixture of mercuric chloride and mercury. It is insoluble in water and is used in medicine. For vapour density reasons the empirical formula HgCl is doubled.

Mercurous Iodide, Hg_2I_2 , is a green powder made by grinding iodine in a mortar with excess of mercury.

Mercurous Nitrate, HgNO_3 or $\text{Hg}_2(\text{NO}_3)_2$, is made by dissolving mercury in cold dilute nitric acid. It is a crystalline salt which is partly hydrolysed by water, forming an insoluble basic compound. It should therefore be dissolved in water containing a little nitric acid.

Mercurous Sulphate, Hg_2SO_4 , is formed when excess of mercury is heated with sulphuric acid.

Mercuric Compounds

Mercuric Oxide, HgO , is produced by long heating of mercury in air or by heating mercuric nitrate.



It is made commercially by heating a mixture of mercuric nitrate and mercury. Mercuric oxide, when heated, darkens,

becoming almost black, and on cooling regains its original colour. At a red heat it decomposes into mercury and oxygen. It is also formed as a yellow precipitate when caustic soda is added to a solution of a mercuric salt. The difference in colour may be due to a difference in crystalline form or grain size

Mercuric Chloride, HgCl_2 , or *corrosive sublimate*, can be made by heating mercury in a stream of chlorine. It is also prepared by heating mercuric sulphate with sodium chloride, the mercuric chloride sublimes as a white powder. Mercuric chloride is a deadly poison; the best antidote is albumen, white of egg, which forms with it an insoluble compound.

Mercuric Iodide, HgI_2 , is formed when mercury is rubbed in a mortar with excess of iodine; also by adding potassium iodide to a solution of mercuric chloride. It appears first as a yellow precipitate which changes to red, and on addition of excess of potassium iodide dissolves. Mercuric iodide is dimorphous. On gentle heating it turns yellow, but when rubbed changes back to the red or stable variety.

Mercuric Nitrate, $\text{Hg}(\text{NO}_3)_2$, is made by dissolving mercury in hot strong nitric acid.

Mercuric Sulphate, HgSO_4 , is a white solid formed when mercury is heated with strong sulphuric acid.

Mercuric Sulphide, HgS , is found naturally as a red ore, *cinnabar*. It also appears as a black precipitate when hydrogen sulphide is passed through a solution of a mercury salt. When the black form is sublimed it changes into the red, and is used as a paint called *vermilion*, which is made commercially by heating mercury and sulphur together and subliming the product.

Tests for Mercury

1. Add hydrochloric acid to the solution. Mercurous salts give a white precipitate of mercurous chloride, which is blackened by the addition of ammonia solution. Mercuric salts give no precipitate.

2. Add sodium hydroxide. A black precipitate of mercurous oxide indicates a mercurous salt, an orange precipitate of mercuric oxide shows a mercuric salt.

3. Add stannous chloride. Mercurous salts give a grey precipitate of metallic mercury. Mercuric salts are first reduced to white mercurous chloride, then to grey metallic mercury.

4. Add potassium iodide. A green precipitate shows a mercurous compound and a red precipitate a mercuric compound. Both precipitates are soluble in excess.

5. Add hydrogen sulphide. With mercurous solutions an immediate black precipitate is obtained; with mercuric solutions the precipitate is first white, then yellow, brown, and finally black.

6. A piece of copper or iron placed in a solution of a salt of mercury becomes coated with a grey deposit of mercury.

7. Any compound of mercury mixed with sodium carbonate and heated in a closed tube gives a grey mirror consisting of small globules of mercury. These can be collected and removed by rubbing with a glass rod covered with filter paper.

QUESTIONS

1. Mention two of the naturally occurring compounds of zinc. Describe the uses of zinc in coating other metals. Why is zinc used for this purpose?

2. Starting from metallic zinc, how would you prepare pure specimens of (a) zinc sulphate, (b) zinc carbonate, (c) zinc oxide? Describe reactions which show that this last compound exhibits both basic and acidic properties. (Scot. Univ. Entrance.)

3. How does mercury occur in nature? Give a short account of the extraction of the metal from the ore.

4. Describe exactly what happens when (1) mercury is warmed with an excess of nitric acid, (2) the solution is evaporated to dryness, (3) the dry residue is heated gently, (4) the product of (3) is heated to bright redness. Give equations. (London Matric.)

5. Explain what is meant by the term amalgam, and mention some of the uses of metallic mercury.

CHAPTER XXXIX

ALUMINIUM AND LEAD

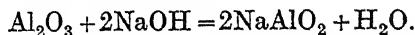
Aluminium. Symbol Al. Atomic weight 27.1. Melting point 657° . Specific gravity 2.7.

History. The name aluminium is derived from the Latin *alumen*, a general term applied to substances with an astringent taste like alum. Alum was well known to the ancient chemists, who classed it as a vitriol and considered that its base was lime. In 1754 Marggraf obtained a new earth, *alumina*, from clay, and showed that it was entirely different from lime. Davy attempted, unsuccessfully, to isolate metallic aluminium by electrolysis, but in 1827 Wöhler succeeded in obtaining it as a grey powder by heating anhydrous aluminium chloride with potassium. Many attempts were made to extract aluminium from the oxide, Al_2O_3 , but it is so difficult to decompose that it was only when electrical processes were introduced into metallurgy that the metal began to be produced cheaply and on a large scale.

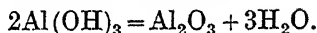
Occurrence. Next to oxygen and silicon, aluminium is the most abundant element in nature. As the oxide, Al_2O_3 , it is found in the *sapphire* and the *ruby*, which are coloured by other metallic oxides. Aluminium occurs chiefly as silicate in *clay*, *slate*, and *felspar*. The ores used in its extraction are *bauxite*, a hydrated oxide, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, found in Ireland, France, and the U.S.A., and *cryolite*, a double fluoride, $3\text{NaF} \cdot \text{AlF}_3$, found in Greenland.

Extraction. The electrolytic process is now practically the only one used in the production of aluminium. The oxide, alumina, is too difficult to melt, m.p. 2000° , but C. M. Hall discovered in 1886 that when alumina is dissolved in molten cryolite the melting point is lowered to about 900° and the solution can be electrolysed, setting free aluminium and oxygen.

The first step in the process is the preparation of pure alumina. Bauxite, which usually contains oxide of iron, is calcined to drive off water and destroy organic matter. It is then heated under pressure with sodium hydroxide solution, and is transformed into soluble sodium aluminate, NaAlO_2 ; the iron remains insoluble as oxide.



The mass is filtered, and the filtrate containing the sodium aluminate is agitated with some aluminium hydroxide, the result being that by a reverse action the aluminate is converted into insoluble aluminium hydroxide. This is filtered off and calcined, obtaining pure alumina.



The second stage is the electrolysis. The electrolytic cell is an iron box lined with gas carbon. The anodes consist of rods of carbon dipping into the bath, and the carbon lining forms

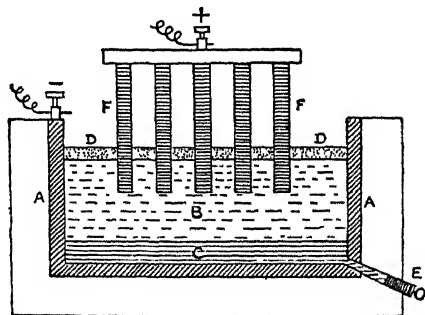


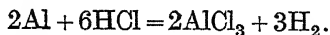
FIG. 108.

- | | | |
|------------------------------|-----------------|------------------|
| A. Carbon Lining. | B. Electrolyte. | C. Aluminium. |
| D. Layer of Powdered Carbon. | E. Taphole. | F. Carbon Anodes |

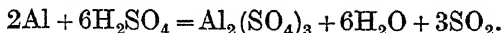
the cathode. Cryolite is melted in the cell and alumina added gradually as required. The molten aluminium collects at the bottom of the cell and is run off at intervals.

Properties of Aluminium. It is a white metal, both malleable and ductile, and takes a high polish. It has a strong attraction for oxygen, but on exposure to air becomes covered with a thin film of oxide which protects it from further attack. When heated in the form of powder or foil it burns with a

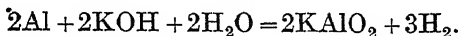
brilliant white flame. Nitric acid has no action on aluminium. It dissolves readily in hydrochloric acid, giving the chloride and hydrogen.



Hot strong sulphuric acid dissolves it, giving the sulphate and sulphur dioxide.



It is also soluble in caustic alkalies, with formation of aluminates and evolution of hydrogen.



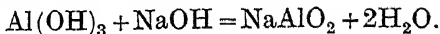
Uses. Used in the form of powder, aluminium reduces metallic oxides on heating. A mixture of powdered aluminium and ferric oxide is used for welding under the name of *Thermit*. The joint to be welded, say two steel rails, is covered with the *Thermit* mixture and ignited by means of a piece of burning magnesium ribbon. The intense heat given out by the combustion fuses the pieces of metal together, giving a very strong joint.

Aluminium powder is a constituent of the explosive *ammonal*, and is also used as a metallic paint. The chief uses of the metal are in the construction of air-craft, on account of its lightness, and in making cooking and other household utensils. It is particularly suitable for the latter purpose, as its salts are not poisonous. Aluminium is a component of many useful light alloys. Aluminium bronze, which contains 90% of copper and 10% of aluminium, is very resistant to corrosion. Duralumin and magnalium, which consist mainly of aluminium, have already been mentioned.

Compounds of Aluminium. The metal is trivalent in its compounds, forming only one series of salts.

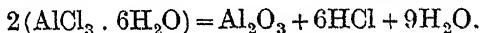
Aluminium Oxide or Alumina, Al_2O_3 . This is prepared by the ignition of the hydroxide $\text{Al}(\text{OH})_3$. It is found naturally occurring as *corundum*, an extremely hard stone, an impure variety of which is called *emery* and is used as an abrasive. Corundum, when coloured by the presence of other metallic oxides, forms the precious stones, *ruby* (red), *emerald* (green), *sapphire* (blue), and others. These are now made artificially by melting alumina and adding an oxide which gives the required colour.

Aluminium Hydroxide, $\text{Al}(\text{OH})_3$. When ammonium hydroxide is added to a solution of an aluminium salt, a precipitate of white gelatinous aluminium hydroxide comes down, insoluble in excess of the precipitant. Caustic alkali gives the same precipitate, but soluble in excess of alkali, forming an aluminate.



Aluminium hydroxide when dissolved in acids gives aluminium salts. Aluminium oxide, like zinc oxide, is therefore amphoteric.

Aluminium Chloride, AlCl_3 , can be prepared anhydrous by heating aluminium in chlorine gas. If the metal is dissolved in hydrochloric acid, the crystalline hydrated salt, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, is obtained, which decomposes easily on heating.



Aluminium Sulphate, $\text{Al}_2(\text{SO}_4)_3$. This salt can be made by dissolving the hydroxide in sulphuric acid and crystallising. Aluminium sulphate forms with the sulphates of the alkali metals a series of double salts called *Alums*; they have been discussed on p. 267

Aluminium Silicates. These occur naturally in clay, slate, etc. *Kaolin*, a china clay, has the composition,



and is used for the manufacture of porcelain and the more expensive kinds of china. Common clay is made into bricks, tiles, pipes, and earthenware vessels. As earthenware is porous, if it is required to hold liquids it must be glazed. This is often done by spraying the articles with a mixture of silicates which melts when the earthenware is fired, and fills up the pores. Common salt and red lead are also used for the same purpose.

A double silicate of sodium and aluminium containing sulphur occurs naturally as *lapis lazuli*, a beautiful blue stone. It is made artificially from kaolin, sodium carbonate, sulphur and charcoal, and is used for artists' colours and laundry blue, under the name of 'ultramarine.'

EXPT.—Test the action of acids and alkalies on aluminium.

EXPT.—Make potash alum by crystallising a mixture of potassium sulphate and aluminium sulphate. Oxidize ferrous sulphate by the addition of sulphuric acid and hydrogen peroxide, and mix with the proper quantity of potassium sulphate to get iron alum.

EXPT.—To show the oxidation of aluminium. Warm a piece of aluminium foil in a solution of mercuric chloride until the surface of the metal shows that amalgamation has taken place. Wash the foil, dry with filter paper and hold it in the hand. Note the evolution of heat as the metal becomes oxidized. Dip a small piece of aluminium in mercury for a short time and observe the sprouting growths of oxide when it is exposed to the air.

EXPT.—Thermit. Place in a clay crucible an intimate mixture of ferric oxide and aluminium powder. On top of this place a small heap of a mixture of sodium peroxide and aluminium powder, in which stick a piece of magnesium ribbon. Ignite the ribbon. A violent reaction follows, and the ferric oxide is reduced to metallic iron. Manganese oxide may also be used.

Tests for Aluminium

1. Add ammonium hydroxide to a solution of aluminium sulphate. A white precipitate appears, insoluble in excess.
2. Add sodium hydroxide; a white precipitate comes down, soluble in excess.
3. An aluminium salt, heated on a charcoal block with the blowpipe, moistened with cobalt nitrate solution and reheated, gives a blue mass.

Lead

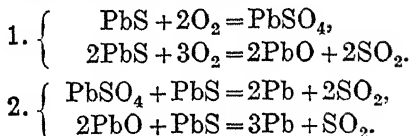
Lead. Symbol Pb. Atomic weight 207.2. Melting point 327° . Specific gravity 11.3.

History. Lead was known to the ancient Egyptians, and is mentioned several times in the Old Testament. The Romans obtained both lead and tin from Britain, but the two metals seem to have been confused, as Pliny (A.D. 77) mentions *plumbum nigrum* and *plumbum candidum*, 'black lead' and 'white lead'. The alchemists connected lead with the planet Saturn and assigned to it the symbol for Saturn, the scythe, ♄ .

Occurrence. The most abundant ore of lead is *galena*, the sulphide, PbS . Next in importance come *cerussite*, PbCO_3 , and *anglesite*, PbSO_4 . Lead ores are found in England, Scotland, the U.S.A., and many other countries.

Extraction. Galena is heated in a current of air at a low temperature, and is oxidized partly to lead sulphate, PbSO_4 , and partly to oxide, PbO . Some more galena is then added, the temperature is raised, and the unchanged galena reacts with

the sulphate and oxide, producing metallic lead. The following equations represent the two stages.

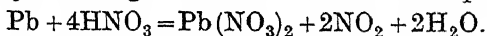


In another process the galena is roasted to oxide, then mixed with coke and smelted in a blast furnace.

Crude lead contains silver. This may be separated by the Parkes process. The lead is melted, and pieces of zinc are thrown in and well stirred. The zinc collects all the silver, forming an alloy with it which floats as a crust on the surface and is skimmed off. On heating this alloy the zinc is volatilised and silver with a little lead is left. The silver is finally purified by heating on a dish made of bone ash known as a *cupel*. A blast of air is blown across its surface, and the lead is oxidized to *litharge*, which is absorbed by the bone ash, leaving a button of silver.

Properties of Lead. It is bluish grey in colour, with a bright metallic lustre when freshly cut, which soon becomes dulled by oxidation. It is soft, without tenacity, but malleable. Exposure to the atmosphere has little effect on it, as it is protected by a thin film of oxide. Heated in air, it is oxidized to *litharge*, PbO.

Nitric acid readily dissolves lead, but dilute hydrochloric and sulphuric acids have little action, as the metal becomes protected by a coating of insoluble chloride or sulphate.



Water, particularly pure soft water from moorland ground, attacks lead and dissolves it. As lead salts are poisonous, it is necessary in such cases to filter the water through limestone. The water takes up a little calcium carbonate, which forms a protective coating on the inside of the lead pipe.

Uses of Lead. On account of its malleability and resistance to corrosion, lead serves many useful purposes. It is used in making lead pipe, roof coverings, tanks, lead chambers in sulphuric acid works, bullets, shot, etc. Lead pipes were formerly made by bending lead sheet into the form of a pipe and soldering the joint, but are now manufactured by forcing the metal in a semi-liquid state through a steel die.

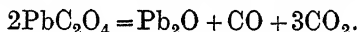
Alloys of Lead. Type metal is an alloy of lead and antimony. When cast it expands on solidification and takes a sharp impression of the mould. Plumbers' solder consists of tin and lead, and has the property of remaining plastic for some time after melting, which enables the plumber to work it round a joint, the process technically known as 'wiping a joint.' Pewter is another alloy of lead and tin. Lead is also the chief metal in many 'bearing metals,' used for machine bearings.

Compounds of Lead

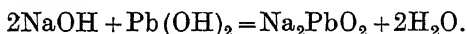
Oxides of Lead. Five of these are known.

Lead suboxide	-	-	-	Pb ₂ O.
Lead monoxide	-	-	-	PbO.
Lead tetroxide	-	-	-	Pb ₃ O ₄ .
Lead sesquioxide	-	-	-	Pb ₂ O ₃ .
Lead peroxide	-	-	-	PbO ₂ .

Lead Suboxide, Pb₂O, is made by heating lead oxalate to 300°.

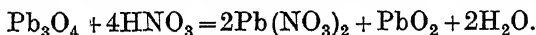


Lead Monoxide or Litharge, PbO, is produced as a yellow powder when lead is heated in air. As we have seen, it is formed when silver is purified from lead by *cupellation*, and on this account received the name *litharge* or 'silver stone.' Litharge dissolves in acids, giving lead salts. When caustic soda is added to a solution of a lead salt, white lead hydroxide is precipitated which dissolves in excess of alkali, giving sodium plumbite, Na₂PbO₂.



Thus lead monoxide is amphoteric. It is used in the manufacture of glass and paint, and as a glaze for earthenware.

Lead Tetroxide or Red Lead, Pb₃O₄, is also known as *minium*. It is prepared by heating lead monoxide or carbonate for a considerable time in air, at a temperature not over 450°. When heated higher it decomposes into litharge and oxygen. Red lead is a scarlet powder which darkens on heating. Dilute nitric acid acts upon it, giving lead nitrate and lead peroxide,



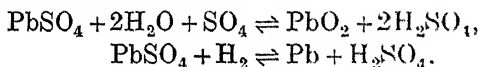
This reaction gives support to the view that red lead may be a compound of lead monoxide and lead peroxide, with the

formula $2\text{PbO} \cdot \text{PbO}_2$. Red lead is used as a paint, in glass-making, and as a cement in making steam joints.

Lead Sesquioxide, Pb_2O_3 . When sodium hypochlorite is added to a solution of litharge in caustic potash, an orange precipitate of the sesquioxide is obtained.

Lead Peroxide, PbO_2 , may be prepared by the action of dilute nitric acid on red lead; a brown residue of lead peroxide is obtained on filtration. It can also be made by adding bleaching powder to a solution of lead acetate. When an acid solution of a lead salt is electrolysed, a dark brown deposit of lead peroxide forms on the anode. This is an exception to the rule that the metal goes to the cathode. Lead peroxide is a powerful oxidizing agent. When ground in a mortar with sulphur it glows, and also becomes incandescent when a stream of hydrogen sulphide or sulphur dioxide is directed on to it.

The Accumulator or Storage Battery. The anode and the cathode are lead plates coated with a paste of red lead and concentrated sulphuric acid. They are immersed in dilute sulphuric acid. When a charging current is passed through the cell from anode to cathode, the SO_4 ion of the sulphuric acid oxidizes the anode to lead peroxide and the hydrogen ion reduces the cathode to metallic lead,



When the accumulator ‘gasses,’ the reactions are complete. On connecting the plates by means of a wire, a current flows in the opposite direction through the wire, and the reverse reaction takes place, both plates becoming coated with lead sulphate.

Lead Chloride, PbCl_2 , is obtained as a white precipitate when hydrochloric acid is added to a solution of a lead salt. It dissolves in hot water and crystallises out on cooling.

Lead Nitrate, $\text{Pb}(\text{NO}_3)_2$, is a white crystalline solid made by dissolving lead or litharge in nitric acid and crystallising.

Lead Carbonate, PbCO_3 . When sodium *bicarbonate* is added to a solution of a lead salt, this compound comes down as a white precipitate. If *normal* sodium carbonate is used, the precipitate is a basic carbonate, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, known as ‘white lead.’ White lead is used extensively as a paint, and is an important article of commerce. There are several modern processes of making it, but the product prepared by the Dutch

process, which is hundreds of years old, is still preferred, on account of its superior 'covering' power. That is, the 'Dutch' paint has greater opacity than other makes, so a smaller quantity is needed.

The method of manufacture is as follows. Earthenware pots are partly filled with vinegar, above the level of which there are ledges supporting rolls of thin sheet lead. These pots are placed on a layer of tan bark or manure and covered with boards. Above this another layer of bark or manure is laid, carrying a tier of pots, and this arrangement is repeated until the chamber is filled. The fermentation of the tan bark produces heat which volatilises the vinegar or acetic acid, and also carbon dioxide. The acetic acid acts on the lead, forming a basic lead acetate, and this is transformed by the carbon dioxide into basic lead carbonate or white lead. The process takes about twelve weeks.

EXPT.—The lead tree. Make a solution of lead acetate. Hang a piece of zinc rod with its lower end dipping into the solution and set aside. Examine at intervals the formation of the 'lead tree.' Notice that lead is deposited on lead, and not as a continuous coating on the zinc. How is this explained?

EXPT.—Cupellation of lead silver alloy This may be done in a muffle or in a cupellation furnace.

EXPT.—Prepare lead peroxide by the action of dilute nitric acid on red lead

EXPT.—Reduce a mixture of litharge and sodium carbonate on a charcoal block by heating with the blowpipe.

EXPT.—Test the action of lead on distilled water and on hard water. Clean some strips of lead sheet, first in alkali to remove grease, next in acid, and finally wash with water. Suspend them in the waters for a few days. Take out a little water from time to time and test for lead by passing through it a current of hydrogen sulphide. Observe which kind of water has the greater solvent effect.

Tests for Lead. Take a solution of lead nitrate.

1. Add hydrochloric acid, a white precipitate of lead chloride appears. Pour $\frac{3}{4}$ of it off, dilute with water and boil.
2. Add potassium iodide solution, a yellow precipitate of lead iodide comes down which dissolves on diluting and boiling, and crystallises out in golden spangles on cooling.

3. Add dilute sulphuric acid, a white precipitate of lead sulphate forms.

4. Add potassium chromate solution, a yellow precipitate of lead chromate appears.

5. Pass a stream of hydrogen sulphide gas through the solution, a black precipitate of lead sulphide forms.

QUESTIONS

1. Give an account of the occurrence of aluminium in nature, and indicate briefly how the pure metal is obtained commercially. Discuss the chief properties of aluminium, showing how these have led to the rapidly increasing use of this metal in everyday life.

(Scot. Leaving Cert.)

2. Describe the action of each of the following on aluminium : nitric acid, hydrochloric acid, sulphuric acid, caustic soda, caustic potash, and give equations for these reactions. Mention another metal which is acted upon by caustic alkalies.

3. What is the most important ore of lead ? How is the metal obtained from this ore ? Name three useful alloys which contain lead, and mention the other metals with which it is associated in these.

(Edin. Univ.)

4. Describe the oxides of lead and copper, and explain how they are produced. How could solutions containing these metals be distinguished from each other ?

(Oxford and Camb. School Cert.)

5. Describe two ways of preparing an oxide from lead, and one method of regaining the metal from the oxide. What is the action of nitric acid on (a) litharge, (b) red lead ?

(London Matric.)

6. Suppose that you were given a substance and were told that it was either lead nitrate, lead carbonate, sodium nitrate, or sodium carbonate. Describe fully how you would find out which of these four substances it was.

(London Matric.)

CHAPTER XL

IRON

Iron. Symbol Fe. Atomic weight 56. Specific gravity 7.8. Melting point 1530°

History. The oldest known specimen of iron, a spear head found in an Egyptian pyramid, is supposed to be at least 4000 years old. At that early date iron was probably only a curiosity, but we know that Indian and Assyrian artificers were celebrated for their skill in iron-making as far back as 1000 B.C. The metal was then coming into general use, and a piece of a large iron saw belonging to this period has been discovered in the ruins of ancient Nineveh. One of the first uses of iron was in making weapons of war; probably on this account the alchemists called it Mars, and gave it the symbol ♄, representing the shield and spear of the god of war. The transition from the Bronze Age to the Iron Age took place in Europe between 1000 B.C. and 500 B.C., and the working and use of iron became general during this period in the countries round the Mediterranean.

The earliest forms of iron were malleable iron and steel, the manufacture of which was introduced into Britain early in the fourteenth century, but it was not until the year 1580 that the smelting process for the production of molten iron came into use, the process which with many improvements is used at the present day.

Occurrence. Meteorites contain metallic iron, generally along with nickel and other metals, but iron is always extracted from its compounds or ores, which are found in all parts of the world. The most important ores are the oxides. *Red haematite*, Fe_2O_3 , is a red stone occurring in Cumberland, Spain and North America. Ferric oxide combined with water, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, is called *brown haematite*, and is found in Spain, Germany and America. *Limonite* is also a hydrated ferric

oxide. Magnetic oxide of iron, Fe_3O_4 , exists in Norway in a very pure state as *magnetite*. There are also carbonate ores, such as *spathic iron ore* or *siderite*, which is ferrous carbonate, FeCO_3 , and is sometimes found mixed with clay or coal as *clay ironstone* or *blackband ironstone*. *Iron pyrites*, FeS_2 , is a common ore of iron, but is not used for the extraction of the metal.

The Smelting Process. Iron ore is first calcined to expel moisture and carbon dioxide and burn off organic matter. It

is then smelted in a blast furnace, which is a tower 80 feet high and 20 feet in diameter at its widest part, built of iron plates and lined with firebrick. At the base is the *taphole*, which can be opened to allow the molten iron to run off, and above it the blast pipes or *twyers* enter, carrying the blast of hot air to support combustion. The gases escape through a pipe near the top and are burned in the *Couper stoves*, two brick towers through which the air blast passes to be heated before it enters the furnace. The charge is introduced at the top of the furnace by means of a *cup and cone* arrangement which prevents the escape of gas. It consists of alternate layers of (1) iron ore to provide the iron, (2) limestone to act as a flux, and (3) coke or coal to supply heat and

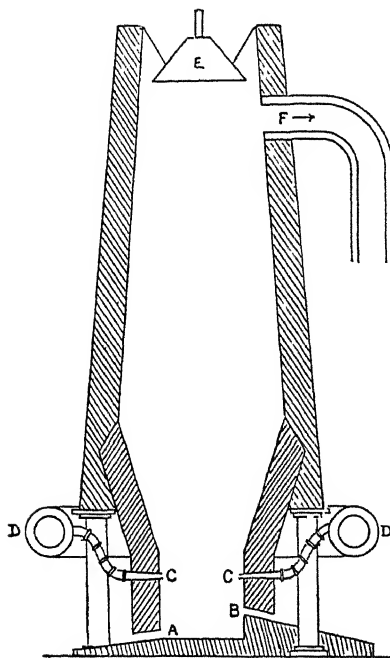
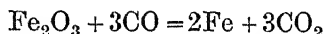


FIG 109—Blast Furnace.

- | | |
|----------------|---------------------------|
| A. Taphole. | B Slaghole. |
| C Twyers. | D. Blast main |
| E Cup and cone | F. Gas outlet or downtake |

produce the carbon monoxide which is the active reducing agent. The limestone breaks up into carbon dioxide and lime, the latter combining chemically with the earthy material,

forming the fusible mixture of silicates known as slag. This floats on top of the molten iron at the bottom of the furnace and runs off continuously through the *slaghole*. The temperature in the hottest part must be over 1200° to melt the iron and slag. The iron oxide is reduced in the upper part of the furnace to metallic iron, which melts and trickles down, collecting at the



base on the hearth. On its way down it dissolves carbon and various elements which have been reduced from their oxides, such as silicon, sulphur, phosphorus, and manganese. When sufficient molten metal has collected, it is run off through the taphole into sand moulds outside the furnace, where it solidifies, giving the blocks known as *pig iron*. The process is continuous.

Pig Iron. There are three varieties of pig iron—grey, mottled and white. In grey iron the carbon is all in the state of free carbon or graphite, which gives the metal its grey colour. In white iron the carbon is combined with iron in the compound carbide of iron, Fe_3C , and mottled irons are intermediate between these two extremes. Pig iron is hard and brittle and cannot be shaped with a hammer. It is used for making wrought iron and steel, and for castings. For the latter it is very suitable, as it has a much lower melting point than pure iron or steel and expands on cooling, thus taking a sharp impression of a mould. It is then known as *cast iron*.

Wrought Iron is made by the *puddling process*. Pig iron is melted in a puddling furnace with oxides of iron such as haematite, which oxidize the impurities carbon, silicon, sulphur, phosphorus and manganese. The carbon is volatilised as carbon monoxide and the others partly volatilise and partly unite with the iron oxide to form a slag. The liberated iron, which is in a pasty condition, as the melting point of pure iron is higher than that of pig iron, is rolled into a ball mixed with slag, which is afterwards squeezed out as far as possible by rolling and hammering. Wrought iron is very pure and resembles steel except for the fact that it contains slag. It is malleable, tough and fibrous, unlike cast iron, and is used for making nails, chains, horse-shoes, anchors, and ornamental ironwork.

Steel. Steel is an alloy of iron and carbon. It is made from pig iron, usually mixed with a proportion of old scrap iron and

steel. The process consists in removing the impurities by oxidation and obtaining a pure metal containing from 0.1-1.5% of carbon, the quantity depending on the purpose for which the steel is required. The hardness of steel increases with the percentage of carbon. Steel containing from 0.1-0.3% of carbon is called *mild steel*.

There are three main processes of steel-making: the Bessemer Converter, the Open Hearth, and the Electric process.

The **Bessemer Converter** is a barrel-shaped furnace supported on piers by means of trunnions, so that it can be rotated at will.

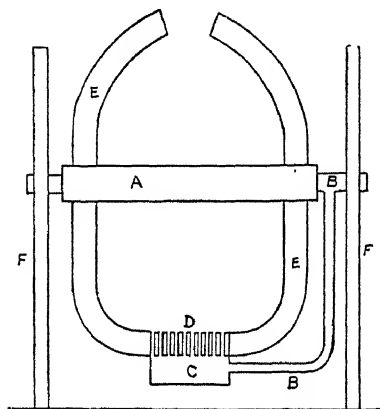


FIG 110 — Bessemer Converter

- | | |
|-------------------|---------------|
| A. Trunnion Belt. | B. Blast Pipe |
| C. Blast Chest. | D. Trwyer |
| E. Lining. | F. Supports |

At the base there is the blast chest into which an air blast is blown and passes into the body of the converter through a number of small openings. The converter is first placed in the horizontal position, and a previously melted mixture of pig iron and scrap iron is poured into it. The blast is then turned on, the converter is rotated into the vertical position, and the air blowing through the molten metal oxidizes the impurities, which go to form a slag. At the same time the iron is oxidized. To correct this, which would render the steel brittle and useless, an alloy of manganese, iron and

carbon is added when the blast is shut off. The manganese deoxidizes the iron, forming manganese oxide, which goes into the slag, and the carbon dissolves in the iron and converts it into steel. The steel is then poured into iron moulds.

The **Open Hearth** steel furnace has a horizontal basin-shaped bed. The charge of pig and scrap is put in cold, and melted down by a gas flame which plays over its surface. The gas is supplied by producers. The impurities in the iron are oxidized both by the air in the furnace and by iron ore which is thrown in at intervals, and manganese is added at the end

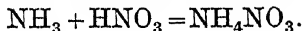
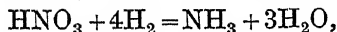
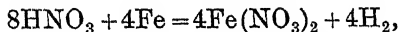
to deoxidize the iron and, provide the necessary carbon. The steel is poured into moulds through a taphole in the bottom of the furnace.

The Electric Furnace. The iron is melted by an electric arc, and oxidation of impurities is effected by iron ore. This process has several advantages. It produces the purest steel; good steel can be made from impure materials, and the composition can be better regulated than by other methods.

Steel is harder than, and not so malleable as, wrought iron, but it possesses much greater strength and can be more cheaply made. Steel containing over 0.5% of carbon can be rendered very hard and brittle by heating to about 800° and dipping into water or oil. If required for tools, the brittleness and part of the hardness is removed by reheating to 200°-300°; this process is known as *tempering*.

Alloy Steels. Many other metals are added to steel, giving alloy steels. Stainless steel, which does not rust, contains 14% of chromium and usually some nickel. Steels with about 4% of nickel and 1% of chromium are very strong and elastic, and are used in motor-car building. Cobalt and tungsten are added to steel to make permanent magnets, while a steel with 25% of nickel is non-magnetic. Tungsten is also used in making *high-speed* lathe tools, which keep their cutting edge even when red-hot. In fact, an alloy steel can be made to suit almost any purpose for which metal is required.

Properties of Iron. It exists in four allotropic modifications, each of which is stable within a definite range of temperature. Iron dissolves in most acids. Dilute sulphuric and hydrochloric acids give ferrous sulphate and ferrous chloride respectively, with evolution of hydrogen. Cold dilute nitric acid gives ferrous nitrate and ammonium nitrate; no hydrogen is evolved. The following equations may help to explain the reaction.



Passivity of Iron. When iron is dipped into concentrated nitric acid it does not dissolve, but is rendered *passive*. In this state it does not behave like ordinary iron; it does not dissolve in dilute acids; it does not precipitate copper from copper sulphate solution or silver from silver nitrate. Passivity is

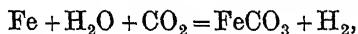
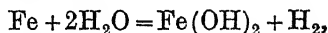
supposed to be due to the formation of a thin film of oxide on the surface of the metal, and is removed by scraping or reduction in hydrogen.

Rusting of Iron. When iron is exposed to a damp atmosphere it becomes covered with a brown coating of rust, which is a mixture of hydroxide and carbonate. Oxygen, moisture, and carbon dioxide are all required for the production of rust. Dry oxygen, or even moist oxygen free from carbon dioxide, does not affect iron, neither does water from which air has been expelled by boiling.

EXPT.—Fill a test tube half full of water, and put in some iron nails which have been brightened by rubbing with emery cloth. Boil the water gently for two or three minutes to expel dissolved gas. Then place a little vaseline in the mouth of the tube, so that it may melt and float on the surface of the water to seal it from air. Take another tube of water and add some clean nails, but do not boil or seal with vaseline. Set the test tubes aside and compare them from day to day.

EXPT.—Place some bright iron nails in a desiccator over calcium chloride or sulphuric acid. The absence of moisture prevents rusting.

When iron rusts, probably ferrous hydroxide and ferrous carbonate are first formed,



and these may afterwards be partly oxidized to the ferric state. The decay of iron by rusting or corrosion is one of its greatest drawbacks. It has been estimated that £500,000,000 worth of metal is annually lost by corrosion. The commonest method of prevention is a coating of paint. In the Schoop process, a molten metal, which may be copper, aluminium, or zinc, is sprayed on to the surface of the iron and forms a very adherent coating. By another method, iron is heated in contact with a powdered metal such as aluminium, which penetrates into it, forming a non-corrosive surface alloy. This process, known as Sherardising, is only applicable to comparatively small objects. Iron is also rendered rustless by the addition of chromium.

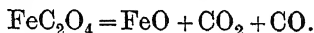
Compounds of Iron. Iron forms two series of compounds, in one of which it has a valency of 2, giving ferrous salts, and in the other a valency of 3, giving ferric salts.

The metal combines directly with many elements. It burns in oxygen, giving the oxide Fe_3O_4 ; in chlorine, giving ferric chloride, FeCl_3 . It unites with sulphur, forming ferrous sulphide, FeS , and with bromine and iodine forms ferric bromide, FeBr_3 , and ferric iodide, FeI_3 .

There are three oxides ferrous oxide, FeO , which is basic and forms ferrous salts; ferroso-ferric oxide, Fe_3O_4 , which is non-basic; and ferric oxide, Fe_2O_3 , basic and forming ferric salts.

Ferrous Compounds

Ferrous Oxide, FeO , is a black powder produced when ferrous oxalate is heated in absence of air.

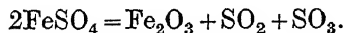


It dissolves in acids, giving ferrous salts.

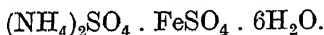
Ferrous Hydroxide, $\text{Fe}(\text{OH})_2$. When sodium hydroxide solution is added to a solution of ferrous sulphate, a white precipitate of ferrous hydroxide comes down. The sodium hydroxide must be previously boiled and the ferrous sulphate dissolved in boiled water, as the white precipitate is rapidly oxidized, first turning green and finally brown.

Ferrous Chloride, FeCl_2 . When iron is dissolved in dilute hydrochloric acid, ferrous chloride is produced. It is easily oxidized to ferric chloride, FeCl_3 .

Ferrous Sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, is known as *green vitriol* or *copperas*, and is the most important ferrous salt. It can be prepared by dissolving iron in dilute sulphuric acid and crystallising. It is made commercially by the slow oxidation of *marcasite* (a variety of iron pyrites). Ferrous sulphate forms green crystals containing seven molecules of water, which on heating lose water, leaving the anhydrous salt FeSO_4 . Stronger heating decomposes it into ferric oxide, Fe_2O_3 , sulphur dioxide and trioxide.



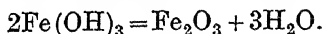
Sulphuric acid was originally made by this method. When ferrous sulphate and ammonium sulphate are dissolved and mixed in molecular proportions, ferrous ammonium sulphate crystallises out on evaporation; it has the formula



A solution of ferrous sulphate is quickly oxidized on exposure to air, but the double salt is much more stable. Ferrous sulphate is used with tannin for making writing ink; it is also used in making Prussian blue and in dyeing.

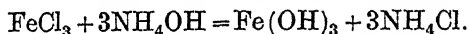
Ferric Compounds

Ferric Oxide, Fe_2O_3 , exists in nature as *haematite*. It can be made by heating ferrous sulphate or ferric hydroxide.



Ferric oxide is a red powder. It is known as *rouge*, and is used for polishing and as a paint.

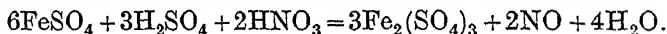
Ferric Hydroxide, $\text{Fe}(\text{OH})_3$. When ammonia is added to a solution of a ferric salt, a brown precipitate of ferric hydroxide appears.



The precipitate is soluble in acids, giving ferric salts.

Ferric Chloride, FeCl_3 , may be prepared in the solid state by heating iron in a stream of chlorine. It is obtained in solution by dissolving ferric hydroxide in hydrochloric acid or oxidizing ferrous chloride with chlorine. On evaporation, yellow crystals of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ are left.

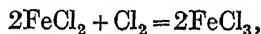
Ferric Sulphate, $\text{Fe}_2(\text{SO}_4)_3$, is produced when ferrous sulphate is boiled with a mixture of sulphuric and nitric acids.



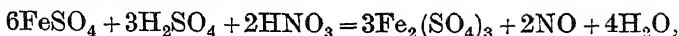
Ferric Ammonium Sulphate or **Iron Ammonium Alum**, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, can be prepared from ferrous ammonium sulphate. Dissolve the salt in water and bring to the boil, add strong nitric acid drop by drop until the brown colour goes and a clear liquid is obtained. Iron alum crystallises out on cooling in violet-coloured crystals.

Ferroso-Ferric Oxide or **Magnetic Oxide**. This oxide is found in nature as *magnetite*. It is formed when iron is heated in air, oxygen or steam. It is a black crystalline substance with magnetic properties and forms no salts. Its chemical behaviour indicates that it is a loosely united compound of ferrous and ferric oxides.

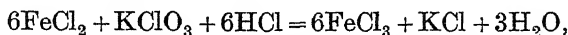
Ferrous salts can be oxidized to the ferric state, by chlorine,



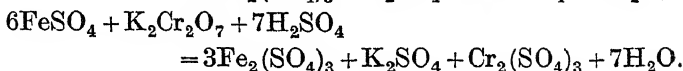
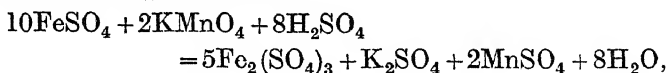
by boiling with nitric acid,



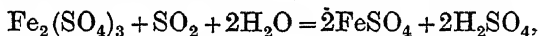
by heating, in the presence of acid, with the addition of a few crystals of potassium chlorate,



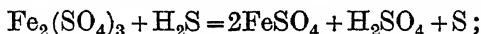
by potassium permanganate and potassium dichromate in the presence of sulphuric acid,



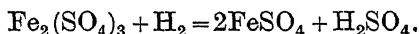
Ferric salts can be reduced, by sulphur dioxide,



by hydrogen sulphide, with precipitation of sulphur,



by zinc and hydrochloric acid (nascent hydrogen),



Tests for Iron

Reagent	Ferrous Iron	Ferric Iron
Ammonium hydroxide	Green to brown.	Brown.
Potassium thiocyanate	No colour.	Red colour.
Potassium ferrocyanide	Light blue.	Dark blue or Prussian blue.
Potassium ferricyanide	Dark blue.	Brown colour.

EXPT.—Dissolve 2 or 3 grams of ferrous sulphate in water, add a little sulphuric acid, and then add potassium permanganate solution of roughly $\frac{N}{10}$ strength till a *faint* pink colour persists. The iron is oxidized to the ferric state. Apply the above tests.

EXPT.—Put 100 c.c. of dilute hydrochloric acid in a beaker. Warm, and add iron filings till no more is dissolved and effervescence ceases. Filter, and test the solution for ferrous iron. Heat the remaining solution to boiling and add strong nitric acid drop by drop, till the liquid turns a yellow colour. Test for ferric iron.

EXPT.—Dissolve a few grams of iron alum in water, or make a solution of it by oxidizing ferrous ammonium sulphate with nitric acid. Add 20-30 c.c. of sulphur dioxide solution till the liquid becomes colourless and smells strongly of the gas. Boil till the odour of sulphur dioxide has disappeared. Cool under the tap and test for ferrous iron.

EXPT.—Make another solution of ferric alum in water, and pass hydrogen sulphide gas through it till a drop taken on a glass rod fails to give a red colour with a drop of potassium thiocyanate on a white tile. Test for ferrous iron.

QUESTIONS

1. Write a short note on the occurrence of iron in nature. Give an account of the method employed in obtaining the metal from the ore. (Scot. Leaving Cert.)

2. Give a brief account of the chemical reactions involved in the extraction of iron from its ores. (London Matric.)

3. Give a brief account of the chief differences between steel, wrought iron, and cast iron. How could you distinguish between ferrous and ferric salts by chemical tests? (Oxford and Camb. School Cert.)

4. What elements are present in (a) steel, (b) bone, (c) china, (d) wood, (e) a sixpence, (f) a diamond? (London Matric.)

5. Describe the preparation and properties of the oxides of iron, and give their formulae. Which of the oxides are salt-forming?

6. Write a short account of each of the following: the rusting of iron, the passivity of iron.

CHAPTER XLI

ATOMIC STRUCTURE

SEVERAL allusions have been made to the modern theories of the structure of the atom, and these theories have created such a revolution in scientific thought that a short account of them is desirable.

Dalton regarded the atom as a hard indivisible particle, a view which for nearly a century after was firmly held by chemists.

Sir W. Crookes in 1870, experimenting with a vacuum tube containing a cathode and anode, found that when the tube was exhausted of air and an electric current passed through it, bluish streams of light proceeded from the cathode and fell upon the glass, producing a green fluorescence. Crookes called these streams of 'radiant matter,' but a full explanation of the phenomenon was not forthcoming till twenty-five years afterwards.

In 1896 Becquerel discovered that a salt of uranium, placed on a photographic plate wrapped in light-proof paper, left an impression on the plate after development. From this he concluded that uranium gave off rays which, unlike sunlight, could penetrate through black paper and even through thin sheets of metal.

Shortly after, in 1898, came the discovery of the wonderful substance Radium, by Madame Curie, afterwards Professor of Physics at the Sorbonne in Paris. She extracted it from pitchblende, a ton of which contains only a fraction of a gram of radium. Radium is a metal which forms salts resembling those of barium, and is usually employed in the form of radium bromide. It has the extraordinary property of giving off continuous radiations of three kinds, α , β and γ . The α -rays are positively charged particles, having a mass four times that of the hydrogen atom and moving at the rate of about 10,000

miles a second. The β -rays are negatively charged particles called **Electrons**, and have $\frac{1}{1836}$ of the mass of a hydrogen atom; they have a velocity approaching the speed of light. The γ -ray is not a particle, but resembles a ray of light of very short wave-length. It has been shown that these rays are produced by the disintegration of the radium atom. Some other elements also show radioactivity.

Radium has been found very useful, in skilled hands, for the treatment of cancer, but it has an extremely destructive effect on the tissues of the body, owing to the continuous bombardment by the penetrating rays, and must be used with great care. Many of the early investigators suffered from painful and incurable wounds, and some indeed lost their lives as the result of their researches in radioactivity.

EXPT.—A simple experiment shows the radioactivity of thorium. A gas mantle (which consists mainly of thorium oxide) is burnt off, cut open with a pair of scissors, and pressed flat on a sheet of cardboard. On top of it is laid a photographic plate wrapped in light-tight paper. After standing two or three weeks, the plate is developed and an image of the mantle is obtained.

Two years before the discovery of radium, the distinguished English physicist, Sir J. J. Thomson, had shown that Crookes' 'radiant matter' consisted of negatively charged particles, which came from the atoms of the metal cathode and were found to be identical with the electrons given off by radium. A new field of research of boundless possibilities was now open to scientists. One discovery followed quickly upon another, and to-day it is known for certain that the atom is not a hard indivisible particle, as was previously supposed.

What electricity is made of we do not know, but we know that the atom, and therefore all matter, is wholly composed of electricity. The atom resembles our solar system on a very minute scale. At the centre there is a **Nucleus**, in which all the weight of the atom is concentrated, composed of unit particles of positive electricity or **Protons**. Each of these has the mass of a hydrogen atom. Round the nucleus at different distances from it, and revolving in their own regular orbits like the planets round the sun, are unit particles of negative electricity, the **Electrons**. Imagine the interior of one of our largest concert halls with a pea suspended in the centre and twenty or thirty midges flying round it at different distances—this will

give you an idea of how the atom would appear to you if you were an electron. It is obvious that most of the atom is empty space; indeed, if the protons and electrons of which our human body is composed were squeezed together until they touched, the bulk would not be as great as the pip of an orange. Astronomers tell us that the star Sirius is made of material which has a density thousands of times greater than the heaviest metal we know.

The number of protons in the nucleus is the **Atomic Weight** of the element, and the number of planetary electrons (the name applied to the electrons which revolve round the nucleus) is called the **Atomic Number**. There are also other electrons in the nucleus which hold the protons together and are known as binding electrons. The simplest atom is that of hydrogen. Its nucleus consists of 1 proton, which has 1 electron revolving round it. The atomic weight and the atomic number are both 1. The carbon atom has 12 protons in the nucleus, corresponding to its atomic weight. Its atomic number is 6, so to balance the electrical charges the nucleus contains 6 electrons, and has a net positive charge of 6. The heaviest atom is that of uranium, atomic weight 238, atomic number 92. The nucleus contains 238 protons and 146 binding electrons, and there are 92 planetary electrons. If the atomic number is subtracted from the atomic weight the number of binding electrons is obtained.

Moseley, a brilliant investigator who was killed in the Great War, devised a method of finding the atomic number of an element, and thus made it possible 'to call the roll' of the elements from the lightest to the heaviest. As the atomic number of successive elements increases by 1, any gap indicates an undiscovered element.

Another unexpected discovery is that atoms of the same element may differ in weight. Atoms which have different weights but the same chemical properties are called **Isotopes**. This accounts for the fact that many elements have atomic weights which are not exactly whole numbers. The weight of each isotope is an exact whole number. Chlorine, for example, is a mixture of three isotopes, a large proportion of the atoms weigh 35, and there are just enough weighing 37 and 39 to make the average atomic weight 35.45. Potassium consists of two isotopes, 39 and 41. Its atomic weight is 39.1, so there is about 5% of isotope of weight 41.

A new kind of hydrogen of weight 2 instead of 1 has been recently discovered. The molecule of water containing ordinary hydrogen is more easily decomposed on electrolysis than that containing heavy hydrogen, so that after long-continued electrolysis the residual water has a higher content of heavy water. Water has been obtained which freezes at 3.8°C. , boils at 101.42° and has a density of 1.1. Heavy hydrogen is said to have poisonous properties.

There is no doubt that there is a large store of energy locked up in the atom, and scientists have held out hopes that if it could be released in usable form we should have a source of power far exceeding that obtainable from the combustion of coal or oil. These hopes, however, have not yet been realised. Some have feared that this energy if released might be uncontrollable, that all the atoms composing this world might disintegrate in a moment and the result 'be advertised to the universe at large as a new star.' Lord Rutherford, who has succeeded in breaking up some of the atoms, has, however, assured us that we may sleep in our beds without fear, as the energy liberated is after all of a very low order.

CHAPTER XLII

THE PERIODIC SYSTEM

THE chief difficulty which perplexes students of Chemistry, more particularly students of Inorganic Chemistry, is perhaps the want of classification. The science seems to us to be, to a great extent, a collection of unrelated facts which make too great demands upon the memory and too little upon the reasoning faculties. It is true that there are certain well-defined classes of substances, acids, bases, salts, metals and non-metals, but we feel the need of a more comprehensive scheme of classification, which will include all the elements and give us a general view of their relationships. Many attempts have been made along these lines.

In 1863 J. Newlands published his *Law of Octaves*. He arranged the elements in order of their atomic weight, and found that they fell naturally into groups of seven, that the properties of every eighth element were a repetition of those of the first, resembling, as he pointed out, the repetition of the octave in music. At that time, however, many of the elements had not been discovered, and atomic weights had not been accurately determined. As a consequence, Newlands' 'Law' did not fit the accepted facts in many details, its importance was not recognised, and it failed to meet general approval.

About 1869 the Russian chemist Mendeléeff published independently a new classification of the elements, which he called the *Periodic Law*. It was based on the principle that 'the elements, if arranged in increasing order of their atomic weights, show a periodicity of properties.' His table, in its latest form with the addition of elements since discovered, and the atomic numbers, is given on next page.

The vertical columns are *groups* and the horizontal rows of elements are *periods*. Looking at the table, we observe that hydrogen is placed alone, as it does not fall naturally into any

PERIODIC CLASSIFICATION

GROUP	VALENCY												VIII
	0	I	II	III	IV	V	VI	VII					
1		+1	+2	+3	+4	+5	+6	+7				+8	
					-4	-3	-2	-1					
		I											
		H 1.008											
2	2	3	4	5	6	7	8	9					
	He 3.99	Li 6.94	Be 9.1	B 11.0	C 12.0	N 14.01	O 16.0	F 19.0					
	10	11	12	13	14	15	16	17					
3	Ne 20.2	Na 23.0	Mg 24.32	Al 27.1	Si 28.3	P 31.04	S 32.07	Cl 35.46					
	18	19	20	21	22	23	24	25					
	A 39.88	K 39.1	Ca 40.07	Sc 44.1	Ti 48.1	51.0 V	52.0 Cr	54.93 Mr				26 Fe 55.84 27 Co 58.97 28 Ni 58.68	
4		29	30	31	32	33	34	35					
		63.57 Cu	65.37 Zn	69.6 Ga	72.5 Ge	As 74.96	Se 79.2	Br 79.92					
	36	37	38	39	40	41	42	43				44 Ru 101.7 45 Rh 102.9 46 Pd 106.7	
5	Kr 82.92	Rb 85.45	Sr 87.63	Yt 89.0	Zr 90.6	93.5 Nb	96 Mo	99 Ma					
		47	48	49	50	51	52	53					
		107.88 Ag	112.4 Cd	114.8 In	119.0 Sn	Sb 120.2	Te 127.5	I 126.92					
6	54	55	56	57	72	73	74	75					
	Xe 130.2	Cs 132.81	Ba 137.37	La 139.0	Hf 178.6	181.0 Ta	184.0 W	186.3 Re				76 Os 190.9 77 Ir 193.1 78 Pt 195.2	
		79	80	81	82	83	84	85				Vg	
7		197.2 Au	200.6 Hg	204.0 Tl	207.1 Pb	Bi 208.0	Po						
	86	87	88	89	90	91	92						
	Rn 222.4	Alb	Ra 226.4	Ac 226.0	Th 232.4	Pa 230	U 238.45						

Fig. 111.

PERIOD

group. After hydrogen there is a 'short' period of eight elements, beginning with helium and ending with fluorine. A new 'short' period then begins with neon, and we observe the resemblances between sodium and lithium, magnesium and beryllium, aluminium and boron, silicon and carbon, phosphorus and nitrogen, and chlorine and fluorine. The repetition of properties occurs at the ninth, not at the eighth element. This is accounted for by the introduction of the inert gases, which had not been discovered when Newlands proposed his theory. Next come two 'long' periods of eighteen elements each, followed by a 'long' period of thirty-two, and finally by a 'short' period of seven elements. Between 57 and 72 there are fourteen elements not shown in the table, called the 'rare earth' metals.

The elements in each vertical group exhibit a similarity of properties. In group 0 there are the inert gases, in group 1 the alkali metals, and so on. In the long periods two elements fall into each group, giving two sub-groups. The members of each sub-group have similar properties, but the properties of one sub-group do not resemble those of the other as a rule. For example, in group 1 the members of the sub-group lithium, sodium, and potassium resemble each other, but do not resemble the members of the sub-group copper, silver, and gold. In each group the metallic character of the element increases towards the bottom of the column.

Again, if we look at the elements in each period, we find that there is a gradual loss of metallic properties from the metals in group 1 to the non-metals in group 7. The positive valency of the elements increases from left to right, from 1 to 7. The negative valency is highest in the middle of the period and then decreases. Thus the valency towards oxygen, or positive valency, increases from 1 in the oxide Na_2O , to 7 in the oxide Cl_2O_7 . The valency towards hydrogen or negative valency is 4 in methane, CH_4 , then decreases to 1 in hydrofluoric acid, HF . The elements in group 8 are called the *transition* elements, and act as connecting links between the two sections of the long periods.

The specific gravity of the elements increases towards the middle of each period and then decreases. A curve may be drawn plotting atomic weights against atomic volumes. The latter are found by dividing atomic weight by specific gravity. Observe that in this curve the summits are occupied by the

alkali metals, and the valleys by the elements in the middle of the period, and that elements with similar properties occupy positions on corresponding parts of the curve.

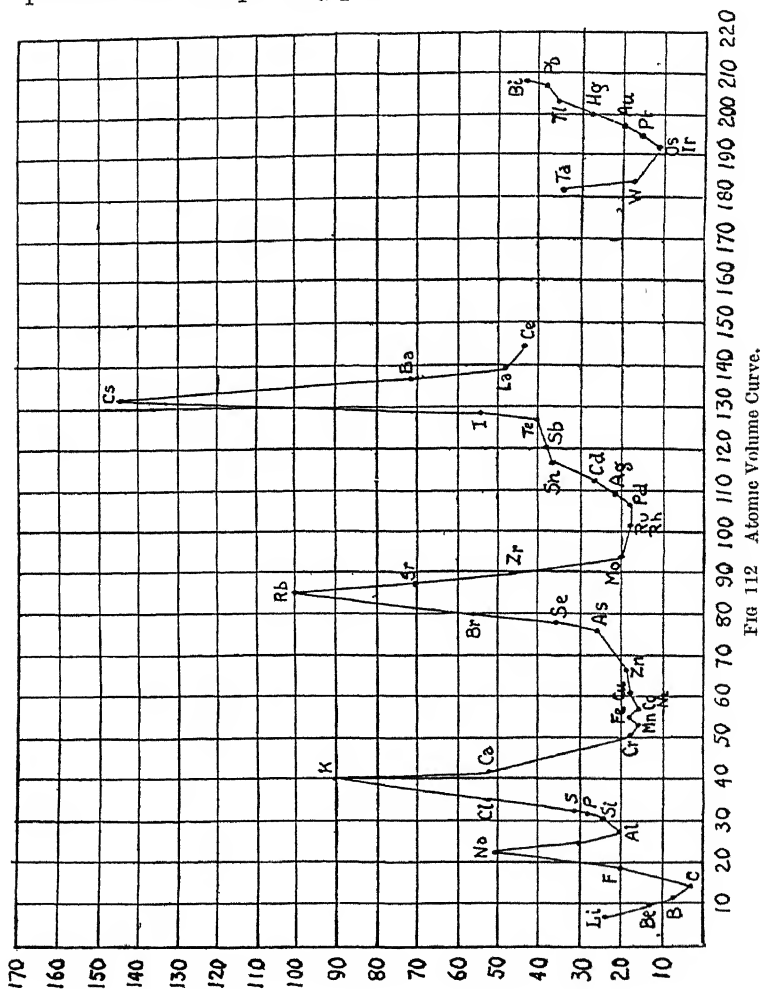


Fig 112 Atomic Volume Curve.

When Mendeléeff constructed his table he left spaces for three undiscovered elements, whose properties he predicted

from a consideration of their position in the table. To these he gave the names of eka-aluminium, eka-silicon, and eka-boron. A few years afterwards the elements gallium, germanium, and scandium were discovered and found to have exactly the properties assigned by Mendeléeff to his imaginary elements.

The periodic classification has led to the correction of the atomic weights of some of the elements which did not fit into their proper places in the table; among these were beryllium, indium, gold, and uranium. It has also been exceedingly useful to investigators in showing by its blank spaces where new elements might be expected, in indicating their probable properties and suggesting methods for their isolation.

The search for new elements, unless the unexpected happens, appears now to be at an end. All the blank spaces in the periodic table are now occupied, but some of the latest comers are waiting a determination of their atomic weights before they are accorded official recognition.

Though the periodic system is the best method of classification which we have up to the present, it is not by any means perfect. The position of hydrogen, or rather the absence of a place in the table for hydrogen, is a difficulty not yet solved. The inclusion of copper, silver, and gold in the same group as the alkali metals, which have such different properties, is unfortunate. Again, there are still two or three elements whose atomic weights do not fit their places in the table. The atomic weight of argon is 39.88, and that of potassium is 39.1. Arranged according to their *atomic weights*, potassium should be among the inert gases and argon among the alkalis. However, if we arrange them according to their *atomic numbers*, $\text{Ar} = 18$, $\text{K} = 19$, they drop into their proper groups. Other examples are cobalt and nickel, atomic numbers 27 and 28; tellurium and iodine, atomic numbers 52 and 53. Another difficulty is the case of the 'rare earth' metals. Between lanthanum and hafnium, atomic numbers 57 and 72, there are fourteen elements called the rare earth metals. They all have a valency of 3, and their properties require that they be placed in group 3.

The atomic number of an element is really the fundamental property which fixes its proper position in the periodic table, so the Periodic Law may be restated thus: 'the elements, if arranged in increasing order of their atomic numbers, show a periodicity of properties.'

QUESTIONS

1. Write a historical account, extending to not more than a page and a half, of the classification of the elements.

(Scot. Leaving Cert.)

2. Show how any five of the following contributed to the development of the science of Chemistry: Boyle; Lavoisier; Dalton; Avogadro; Mendeléeff; Madame Curie.

(Scot. Leaving Cert.)

3. Write a short note on the chemical discoveries or principles associated with any three of the following names: (1) Dumas, (2) Ramsay, (3) Faraday, (4) Black, (5) Mendeléeff, (6) Gay Lussac. Indicate as nearly as you can when and where the above scientists carried out their work.

(Scot. Univ. Entrance.)

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TABLE OF ATOMIC NUMBERS AND
ATOMIC WEIGHTS

(See pages 374-5)

TABLE OF ATOMIC NUMBERS AND ATOMIC WEIGHTS

ELEMENT	SYMBOL	ATOMIC NUMBER	ATOMIC WEIGHT
Aluminium	Al	13	26.97
Antimony	Sb	51	121.76
Argon	A	18	39.94
Arsenic	As	33	74.93
Barium	Ba	56	137.36
Beryllium	Be	4	9.02
Bismuth	Bi	83	209.00
Boron	B	5	10.82
Bromine	Br	35	79.91
Cadmium	Cd	48	112.41
Caesium	Cs	55	132.83
Calcium	Ca	20	40.07
Carbon	C	6	12.00
Cerium	Ce	58	140.13
Chlorine	Cl	17	35.45
Chromium	Cr	24	52.01
Cobalt	Co	27	58.94
Copper	Cu	29	63.57
Dysprosium	Dy	66	162.50
Erbium	Er	68	167.74
Europium	Eu	63	152.0
Fluorine	F	9	19.00
Gadolinium	Gd	64	157.3
Gallium	Ga	31	69.72
Germanium	Ge	32	72.6
Gold	Au	79	197.20
Hafnium	Hf	72	178.6
Helium	He	2	4.00
Holmium	Ho	67	163.5
Hydrogen	H	1	1.008
Indium	In	49	114.8
Iodine	I	53	126.93
Iridium	Ir	77	193.1
Iron	Fe	26	55.84
Krypton	Kr	36	82.9
Lanthanum	La	57	138.9
Lead	Pb	82	207.22
Lithium	Li	3	6.94
Lutecium	Lu	71	175.0
Magnesium	Mg	12	24.32
Manganese	Mn	25	54.93
Masurium	Ma	43	99.0

TABLE OF ATOMIC NUMBERS AND ATOMIC WEIGHTS—*Contd*

ELEMENT	SYMBOL	ATOMIC NUMBER	ATOMIC WEIGHT
Mercury -	Hg	80	200.61
Molybdenum -	Mo	42	91.22
Neodymium -	Nd	60	144.27
Neon -	Ne	10	20.18
Nickel -	Ni	28	58.69
Niobium -	Nb	41	93.1
Niton -	Nt	86	222.5
Nitrogen -	N	7	14.0
Osmium -	Os	76	190.8
Oxygen -	O	8	16.00
Palladium -	Pd	46	106.7
Phosphorus -	P	15	31.02
Platinum -	Pt	78	195.2
Potassium -	K	19	39.10
Praseodymium -	Pr	59	140.92
Radium -	Ra	88	226.4
Rhenium -	Re	75	186.3
Rhodium -	Rh	45	102.9
Rubidium -	Rb	37	85.44
Ruthenium -	Ru	44	101.7
Samarium -	Sa	62	150.4
Scandium -	Sc	21	45.10
Selenium -	Se	34	79.2
Silicon -	Si	14	28.06
Silver -	Ag	47	107.88
Sodium -	Na	11	22.99
Strontium -	Sr	38	87.63
Sulphur -	S	16	32.06
Tantalum -	Ta	73	181.0
Tellurium -	Te	52	127.5
Terbium -	Tb	65	159.2
Thallium -	Tl	81	204.41
Thorium -	Th	90	232.4
Thulium -	Tm	69	168.5
Tin -	Sn	50	118.70
Titanium -	Ti	22	47.90
Tungsten -	W	74	184.0
Uranium -	U	92	238.5
Vanadium -	V	23	50.95
Xenon -	Xe	54	130.2
Ytterbium -	Yb	70	173.5
Yttrium -	Yt	39	88.92
Zinc -	Zn	30	65.38
Zirconium -	Zr	40	91.22

